European Food Safety Authority

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SCIENTIFIC OPINION

Guidance for evaluating laboratory and field dissipation studies to obtain DegT50 values of plant protection products in soil[1]

EFSA Panel on Plant Protection Products and their Residues (PPR)[2, 3]

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ABSTRACT

The European Commission asked the Panel to revise the Guidance Document on persistence in soil (SANCO/9188VI/1997 of 12 July 2000). Therefore the Panel started the development of a revised methodology for the assessment of exposure of soil organisms. This opinion provides guidance on how to derive the half-life for degradation in the top 30 cm of soil at reference temperature and moisture conditions (i.e. 20°C and field capacity) from the results of field studies in which the plant protection product was sprayed onto the soil surface. This half-life is an important input parameter in model simulations of the exposure of organisms in soil for annual crops under conventional and reduced tillage and therefore this guidance is an important part of this revised methodology. The Panel proposes the splitting of field dissipation studies into two parts viz. before and after at least 10 mm of rain has fallen since application. The Panel recommends evaluating field dissipation studies with models capable of considering a biphasic decline and taking only the slow phase of this decline, taken to represent degradation in the soil matrix rather than loss processes from the soil surface, into account for estimating this half-life. If however, surface processes do not seem to occur the Panel proposes to use single first-order kinetics after eliminating data points before 10 mm of rain has fallen. The Panel proposes basing the relevant population of half-lives for a certain soil exposure scenario on the assumption that a half-life measured for any non-volcanic agricultural soil from temperate regions can be used to predict the half-life for any such soil within the EU. The aim is to estimate the geomean half-life of this relevant population. The Panel considers it necessary to include the uncertainty resulting from the sample size of the population in the estimation of this geomean. If the relevant population of half-lives for a certain exposure scenario consists of a mixture of values obtained in the laboratory and in the field, the Panel recommends rejecting the laboratory values only if the null hypothesis that laboratory and field half-lives are equal is rejected. The Panel considers that this guidance will also be useful to determine half-lives to be used in scenario calculations for the assessment of leaching to groundwater and surface water. Should the notifier want to use results of field dissipation studies for estimating

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the half-life in the top 30 cm of soil as an input parameter for exposure models, the Panel recommends incorporating the plant protection product to a depth of about 10 cm in soil immediately after application.

KEY WORDS

field persistence, degradation, dissipation, half-life, accumulation, exposure, soil organisms

SUMMARY

The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) of EFSA was asked in November 2007 by EFSA to prepare a revision of the Guidance Document on persistence in soil (SANCO/9188VI/1997 of 12 July 2000). This revision will consist of a tiered exposure assessment for organisms in soil (for annual crops under conventional and reduced tillage) based on scenarios for analytical and numerical models (EFSA, 2010b). In this exposure assessment, degradation parameters derived from field dissipation and soil accumulation studies are important input parameters for the numerical models. Therefore this opinion aims to provide guidance on best practice for using the results of standard field studies and soil accumulation studies in which plant protection products have been sprayed on the soil surface.

The half-life for degradation in the top 30 cm of soil at 20°C and pF = 2 is an important input parameter for numerical models that simulate exposure of organisms in soil. For soil under conventional or reduced tillage, the main use of this half-life is to simulate the degradation rate for soil depths between 1 and 30 cm. When deriving such a half-life from field dissipation and soil accumulation studies, appropriate measures have to be taken to ensure that the value obtained is not influenced strongly by processes in the top millimetres of soil (such as volatilisation and photodegradation).

Based on current knowledge and data commonly available in dossiers of plant protection products, it is impossible to estimate with enough certainty photodegradation rates of plant protection products in the top millimetres in soil. Studies with sieved soils in the laboratory demonstrate that photodegradation is limited to the top 2 mm of soil. Furthermore there are uncertainties assessing volatilisation for surface-applied compounds.

Current numerical models used for simulating behaviour of plant protection products in soil in the context of the EU regulatory exposure assessment are unable to describe satisfactorily the daily fluctuations of the soil temperature and of the volume fraction of water in the top millimetres of soil.

The parameters describing the relationship between the degradation rate coefficient in soil and the soil temperature (i.e. the Arrhenius activation energy) or the volume fraction of water in soil (i.e. the exponent *B*) show a considerable variation between soils and plant protection products. This uncertainty results in a considerable uncertainty in the degradation half-life within the top 30 cm of soil obtained from field studies by inverse modelling assuming default values of the Arrhenius activation energy and the exponent *B*.

To guarantee that the residues describe the degradation in the soil matrix rather than at the soil surface the Panel proposes the splitting of field dissipation studies into two parts viz. before and after at least 10 mm of rain has fallen since application.

Assessment of degradation half-lives in the top 30 cm of soil derived from field dissipation studies can be based on inverse modelling using the approach of normalised decline curves proposed by FOCUS (2006). The normalised decline curves can be either described with the DFOP (double first-order kinetics in parallel) or Hockey-Stick models.

The Panel considers soil accumulation studies with only two or three soil samplings per year not suitable for estimating the degradation half-life in the top 30 cm of soil because the fraction of the dosage that penetrates to soil depths deeper than a few millimetres cannot be estimated with sufficient accuracy.

Once appropriate degradation half-lives from laboratory and field studies are available, the estimation of the half-life to be used as input for the required exposure scenario consists of two more steps: (i) assess the relevant population of half-life values for the required exposure scenario, and (ii) estimate

reliably the required statistical attribute (certain percentile or some mean value) based on this population. The Panel proposes to base the relevant population of half-lives on the assumption that a half-life measured for any non-volcanic agricultural soil from temperate regions can be used to predict the half-life for any such soil within the EU. This assumption is a working hypothesis that has to be underpinned further. The type of attribute has to be consistent with the scenario-selection procedure which was based on taking the geomean half-life assuming a log-normal distribution. So the Panel recommends taking the geomean half-life. The estimation of the geomean half-life of the population has to consider the uncertainty resulting from the limited number of samples in the sample population.

If the relevant population of half-lives for a certain exposure scenario consists of a mixture of values obtained in the laboratory and in the field, the Panel recommends excluding the laboratory values only if the null hypothesis that laboratory and field values are equal is rejected. If the relevant population of half-lives for a certain exposure scenario consists of less than four values based on field studies, the Panel recommends using both laboratory and field values for estimating the geomean (even if this null hypothesis is rejected).

The Panel considers the guidance proposals for estimating half-lives also useful for assessment of leaching to groundwater and surface water because the main use of the half-lives in these groundwater and surface water scenarios is the same as for the soil exposure assessment considered in this opinion (i.e. simulating the degradation rate for soil depths between 1 and 30 cm).

Some uncertainty in the estimation of the half-lives has been addressed, but the Panel recognizes that further uncertainties exist and recommends that further work be done to evaluate their combined impact on the reliability of the exposure assessment.

However, the Panel is of the opinion that the provision it has made for these uncertainties within the proposed procedures, together with the improved handling of processes in the top millimetres of soil, will mean that the *DegT50* of parent substances will be underestimated only for a small proportion of the substances.

The Panel recommends compiling a database for all substances listed in Annex I of all relevant and reliable half-lives of agricultural top soils within the temperate regions at 20°C and pF = 2 to test the assumption that this half-life does not vary systematically between geographical zones in the temperate regions for non-volcanic soils.

Should the notifier wish to use results of field dissipation studies for estimating the half-life in the top 30 cm of soil as an input parameter for exposure models, the Panel recommends incorporating the plant protection product to a depth of about 10 cm into the soil immediately after application.

The Panel recommends research be conducted to further improve the reliability of mechanistic models for simulating loss processes at the soil surface especially for photodegradation and volatilisation.

The Panel recommends including in future exposure assessment methodologies the uncertainty resulting from the use of the sample geomean to estimate the geomean of the statistical population, and intends to develop approaches for this in a forthcoming guidance.

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BACKGROUND AS PROVIDED BY EFSA

During the review process of the substances of the second list, several concerns were raised regarding the Guidance Document on persistence in soil. A number of Member States have expressed interest in a revision of the current Guidance Document on persistence in soil during the general consultation of Member States on Guidance Documents in answer to the request by the Director of Sciences of EFSA in a letter dated 3 July 2006 sent *via* the Standing Committee on the Food Chain and Animal Health. Furthermore, the EFSA PRAPeR Unit has noted that the Guidance Document needs to be brought in line with the FOCUS degradation kinetics report (SANCO/100058/2005, version 2.0, June 2006).

FOCUS (1997) developed the first guidance at EU level for exposure assessment in soil. This included a simple approach for estimating PEC_{SOIL} but FOCUS (1997) did not develop first-tier scenarios (in contrast to subsequent FOCUS workgroups that developed such scenarios for surface water and groundwater as development of soil scenarios was a lower priority at that time). FOCUS (2006) developed detailed guidance on estimating degradation rate parameters from laboratory and field studies, but did not develop exposure scenarios. Nevertheless there is a need for such scenarios in view of ongoing discussions in PRAPeR experts' groups regarding PEC_{SOIL} as current approaches at EU level only represent the range of climatic conditions covered by available field dissipation and/or accumulation studies, and Member States would like tools to be able to extrapolate to a wider range of climates present in the EU.

The existing Guidance Document on Persistence in Soil (9188/VI/97 rev 8, EU 2000) published in 2000 did not include scenarios. The intention with the new guidance document is to update the existing Guidance Document on Persistence in Soil to include European exposure scenarios for soil and to provide guidance on best practice for using the results of field studies and soil accumulation studies in the exposure assessment.

The revision will not include guidance that is in the existing guidance document but has been replaced by newer guidance e.g. in FOCUS (2006). Some parts of the current guidance will not be considered in the revision, e.g. for soil-bound residues, as these sections are better dealt with separately. The revision will also exclude risk-management guidance and hazard cut-offs e.g. PBT classification as this is not within the mandate given to EFSA.

Member States and stakeholders have been and will be consulted through web-conferences and stakeholder workshops to collect comments during the revision of the Guidance Document.

TERMS OF REFERENCE AS PROVIDED BY EFSA

The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) of EFSA was asked in November 2007 by EFSA to prepare a revision of the Guidance Document on persistence in soil (SANCO/9188VI/1997 of 12 July 2000).

1. Introduction

1.1. Role of field dissipation and soil accumulation studies in the tiered exposure assessment

EFSA (2010a) proposed a tiered approach for the assessment of exposure of organisms to plant protection products[4] in soil after spray applications in annual crops under conventional and reduced tillage. Its purpose is to assess the all-time high (either peak or TWA values) of the spatial 90th percentile concentration resulting from the use of the plant protection product and considering the population of agricultural fields (in one of the three regulatory zones North-Centre-South) where the crop is grown in which this plant protection product is applied (assuming a fraction of the target crop treated of 100%). The tiered approach consists of six tiers, of which five are based on calculations with simple or numerical models (Figure 1; see EFSA, 2010a, for further details of the tiers).

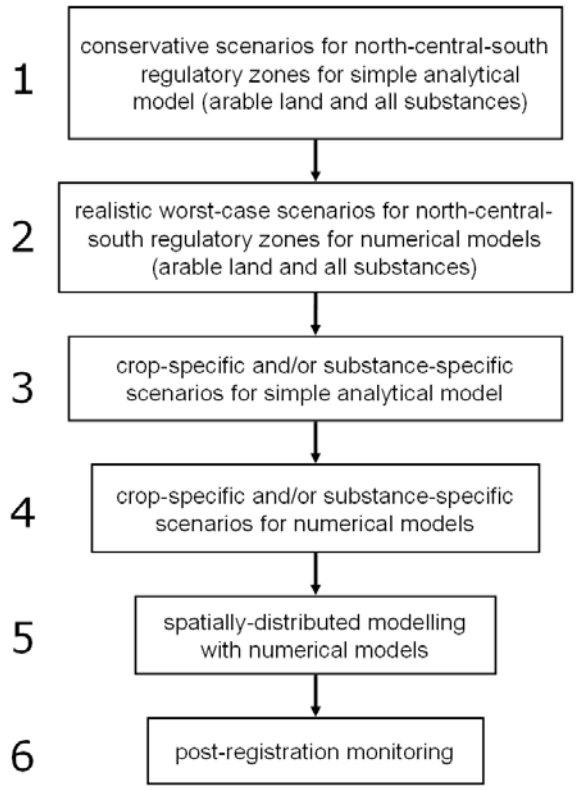

Figure 1: Tiered scheme for the exposure assessment of soil organisms in annual crops with conventional or reduced tillage after spray applications (taken from EFSA, 2010a).

For the exposure assessment in soil, the degradation[5] half-life (*DegT50*) in top soil at 20°C and field capacity (pF = 2) is an important input parameter of the simple and numerical models used in Tiers 1 to 5 (Figure 1). In a dossier there will be usually a minimum of four laboratory studies on the degradation rate. Annex II to Council Directive 91/414/EC[6] requires four field dissipation studies if

[4] In the context of this opinion, the term 'plant protection products' is used for both the applied formulation and the active substances themselves.
[5] The Panel uses in this opinion the definition of 'degradation' (which includes transformation) as suggested by FOCUS (2006).
[6] Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market. OJ L 230, 19.8.1991, p. 1-32.

the degradation half-life (*DegT50*) in top soil at 20°C at pF = 2-2.5 exceeds 60 days. As a consequence, for many plant protection products there are additionally four (or more) field dissipation studies. For persistent compounds (time needed for 90% dissipation in the field longer than 1 year) there may be additionally one or two soil accumulation studies. In principle all these studies may generate *DegT50* values. EFSA (2010a) proposed basing the estimation of the *DegT50* on a stepped approach (Figure 2) for all relevant tiers: (i) considering only values from laboratory studies, (ii) including also values from field dissipation studies and (iii) including additionally values from soil accumulation studies. This is done because field dissipation studies and soil accumulation studies may provide more realistic estimates of this half-life than the laboratory studies.

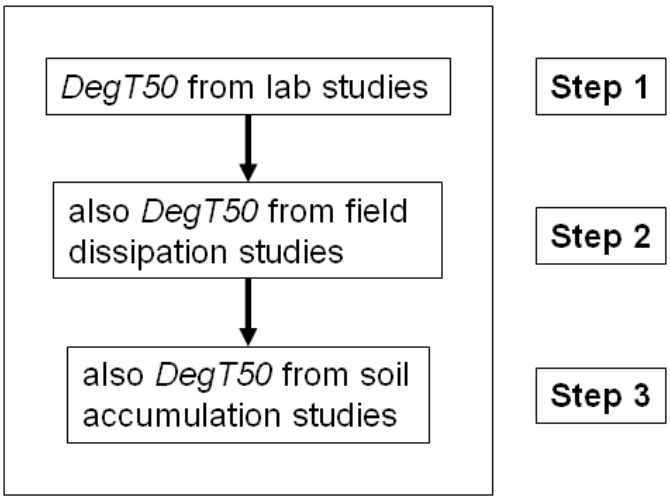

Figure 2: Schematic representation of stepped approach for estimating the *DegT50* in the soil to be used in the tiered exposure assessment (EFSA, 2010a).

This document provides guidance for the assessment of the *DegT50* to be used not only for the soil exposure assessment but also for the assessment of leaching to groundwater and surface water. It would be very confusing if the guidance for the assessment of the *DegT50* were to be different for the various exposure assessments in the EU regulatory process, for the degradation rate of plant protection products in soil also plays an important role in the assessment of such leaching. In the EU simulations of leaching to groundwater, the *DegT50* values are even extrapolated to the 30-100 cm layer by assuming a single and unique relationship between soil depth and *DegT50* for all plant protection products and their metabolites in all soils in EU agriculture (FOCUS, 2000). As a consequence, the concentrations leaching to groundwater are very sensitive to the *DegT50* in the top soil (e.g. a decrease in the *DegT50* of only 10% may lead to significant decreases in calculated leaching concentrations).

It has long been known (Anderson, 1987) that the viability of soil microbial populations decreases with time in laboratory studies. Therefore OECD (2002b) recommended restricting the duration of laboratory studies to 120 days. So field studies may be better suited to measure the degradation rate of persistent substances. A substantial proportion of the parent molecules and metabolites of plant protection products registered at EU level may be so persistent that study duration of 120 d is too short for a good measurement of the degradation rate. As will be explained in detail below, the procedure for estimating the *DegT50* of top soil at 20°C and pF = 2 from field studies is more complicated and has more uncertainties than that from laboratory studies. The Panel proposes to handle these uncertainties by developing a pragmatic procedure. The alternative would be to develop a procedure based on scientifically conservative methodologies. Conservative is defined in the context of this opinion as 'on the safe side with respect to the risk assessment'. The proposed procedure is restricted

to parent molecules. For the exposure assessment of soil metabolites, the Panel recommends a case-by-case approach based on that used for parent compounds.

Considering a certain exposure scenario in Figure 1, the first step is to select the relevant population of studies to be included in the estimation of the *DegT50* value for the required exposure scenario. For example, a *DegT50* value at 20°C and pF = 2 derived from a field study on a heavy clay soil with 10% of organic matter in Finland may perhaps not be considered relevant for estimating the *DegT50* value at 20°C and pF = 2 for a sandy soil with 1% of organic matter in Spain. Once the relevant population of *DegT50* values has been defined, the question is how to derive the *DegT50* value to be used in the exposure assessment from this population. EFSA (2010a) indicated that the *DegT50* should be part of the scenario-selection procedure. EFSA (2010b) developed this scenario selection procedure and they selected scenarios assuming that the median *DegT50* will be used as the input to the scenario calculations. FOCUS (2006; p. 234) recommended using the geometric mean of the *DegT50* values based mainly on the argument that taking the geomean of a number of rate coefficients will give the same result as taking the geomean of the corresponding half-lives. The Panel proposes to use the geomean of the relevant *DegT50* values and considers this to be in line with both EFSA (2010b) and FOCUS (2006) because the median is considered to be a good estimator for the geomean for lognormal distributions (such a distribution is commonly assumed the best guess for quantities that cannot be negative such as the *DegT50*).

As described by EFSA (2010a), there is a complication with respect to the estimation of the individual *DegT50* values from field dissipation studies in which the plant protection product is sprayed onto the soil surface. These *DegT50* values will be used to simulate long-term accumulation of plant protection products with ploughing up to 20 cm depth every year. So they have to reflect the degradation rate within the soil matrix. Field dissipation studies regularly show a fast initial decline (Walker et al., 1983). Immediately after spraying onto the soil surface, the plant protection product is concentrated in the top millimetres of the soil. For example, an application of 1 kg active substance in 250-500 L water per hectare gives a content of 500-1000 mg/kg of this substance in the top 0.1-0.2 mm of soil. In the top millimetres of soil, loss processes other than degradation within the soil matrix may play a significant role (volatilisation, photochemical degradation, runoff etc.). So it has to be ensured that the estimated *DegT50* is not influenced by these loss processes. Additionally, it is not clear whether the degradation rate within the soil matrix in these top millimetres can be safely extrapolated to estimate the degradation rate at depths between 1 and 30 cm (see Chapter 2). Therefore a procedure is needed that ensures that the *DegT50* derived from field dissipation studies reflects the degradation rate within the soil matrix between 1 and 30 cm depth with sufficient accuracy. This *DegT50* within the soil matrix in the 1-30 cm layer of soil will be further called $DegT50_{matrix}$. Thus the measured decline has to be split into two parts, one reflecting the behaviour in the top millimetres and the other reflecting the behaviour in deeper soil.

This interpretation problem with respect to the decline in the top millimetres applies also to soil accumulation studies. However, for these studies there is an additional complication. They may contain only two to three samplings per year and the plant protection product may have been sprayed on a full-grown crop. In such a situation it may be difficult to estimate the fraction of the dose that eventually penetrated the soil. This may complicate an accurate estimation of the $DegT50_{matrix}$ from soil accumulation studies. So also here a procedure is needed to ensure that the *DegT50* derived from soil accumulation studies reflects the degradation rate within the soil matrix between 1 and 30 cm depth.

This interpretation problem is relevant for soil exposure assessments in which the concentration endpoint has to be based on multi-year simulations and in which a significant fraction of the dosage penetrates to below 1 cm depth (either by leaching or by soil tillage). This is the case for the soil exposure assessment under conventional and reduced tillage and by definition for the leaching assessment. The relevance of this problem for the soil exposure assessment for no-tillage systems and for permanent crops is not yet clear. This can only be clarified after tiered exposure approaches for no-tillage systems and for permanent crops (similar to the one in Figure 1) have been defined.

This interpretation problem is of no importance if the plant protection product is incorporated into the top 10 cm of soil immediately after application. However, this is not common practice in the field dissipation studies available in the dossiers. It is not clear whether incorporation is a solution also for the no-tillage systems because the tiered approach for the no-tillage systems has not yet been defined.

As stated earlier, it is expected that surface processes may interfere when deriving $DegT50_{matrix}$ values from field studies. Should the notifier wish to use results of field dissipation studies for estimating the half-life in the top 30 cm of soil as an input parameter for exposure models, a different experimental set-up might be applied in order to avoid this interpretation problem. Some options are:

1. incorporation of the substance in the soil immediately after spraying to the soil surface, mixing should be at least over a depth of 10 cm
2. injection of the substance in the (top layer, 0 – 30 cm layer of the) soil and mixing through the soil over a depth of at least 10 cm
3. irrigation immediately after application of the substance to the soil surface; the irrigation depth should be sufficient to reach an average penetration depth of the substance of 10 mm (to be calculated with models such as PELMO and PEARL)

In all cases, the first soil sampling should take place after the incorporation or irrigation has taken place.

At this moment the only guidance to address this interpretation problem is the bullet list on p. 177 of FOCUS (2006). This list describes only in very general terms how to handle initial loss processes. This leads in current EU regulatory practice to rejection of a substantial proportion of the field dissipation studies.

1.2. Aims of this guidance proposal

In view of the foregoing, the aims of this guidance proposal are:

(i) to develop procedures for estimating $DegT50_{matrix}$ values reliably from results of individual field dissipation and soil accumulation studies

(ii) to develop procedures for assessing the relevant population of $DegT50_{matrix}$ values for the required exposure scenario

(iii) to develop procedures for estimating reliably the geomean of the relevant population of $DegT50_{matrix}$ values for the required exposure scenario.

As described in Section 1.1, procedures will have to be developed for splitting the measured decline found in field dissipation studies into the two parts. These procedures will generate as spin-off information on losses from the top millimetres of soil under field conditions (e.g. due to photodegradation or volatilisation). It may be relevant to take this information into account in the exposure assessment. Therefore the Panel aims at additionally developing procedures for using this information in the exposure assessment. This aim can be split up (in analogy with the guidance for the $DegT50_{matrix}$) into:

(i) to develop procedures for estimating decline parameters in the top millimetres of soil reliably from results of individual field dissipation and soil accumulation studies

(ii) to develop procedures for assessing the relevant population decline parameters in the top millimetres of soil for the required exposure scenario

(iii) to develop procedures for estimating reliably the rapidly dissipating fraction from the top millimetres of soil for the required exposure scenario from the relevant population of values.

The processes underlying these declines in the top millimetres of soil were not included in the scenario-selection procedure by EFSA (2010b). Therefore the Panel considers it not justifiable to use, for example, geomean or median values of the top-soil decline parameters. Instead this endpoint of the top-soil decline parameters should be a kind of worst case.

1.3. Bird's eye view of opinion

Chapter 2 describes the background of the problems of using measured declines in the top millimetres of soil for estimating the $DegT50_{matrix}$ and provides a proposal for the solution of these problems. This proposal is the basis for the guidance for evaluating results from field dissipation studies described in Chapter 3. The Panel made an attempt to develop guidance for soil accumulation studies but this proved not to be feasible (Chapter 4). The next step is to use the available and relevant information from all laboratory and field studies for the exposure assessment in the required scenario (Chapter 5). Finally, the Panel considers the possible usefulness of the developed proposals for another purpose, i.e. the assessment of leaching to groundwater and surface water at EU level (Chapter 6).

2. Background of the problems of estimating the $DegT50_{matrix}$ from measured declines after spraying onto bare soil in field dissipation studies and a proposed solution

2.1. Introduction to the problem

FOCUS (2006) proposed a procedure to derive $DegT50_{matrix}$ values at 20°C and pF = 2 from field dissipation studies via inverse modelling procedures. This procedure is the current guidance for extracting this $DegT50_{matrix}$ value from field dissipation studies which has been applied widely in the EU exposure assessments. However, the Panel has serious reservations with respect to this procedure. These reservations are explained below.

Let us first explain the principles of this inverse modelling procedure. It is generally recognised that the degradation rate in soil is a function of soil moisture, soil temperature and soil depth (FOCUS, 2000). So any $DegT50_{matrix}$ is a function of these three soil properties. The relationship between $DegT50_{matrix}$ and soil moisture content is commonly described by an empirical equation (Walker, 1974):

$$DegT50_{matrix} = DegT50_{matrix,FC}\left(\frac{\theta}{\theta_{FC}}\right)^{-B} \quad (1)$$

where

'FC' = at field capacity, i.e. matric suction of 100 hPa or pF = 2

θ = volume fraction of water in soil (m^3/m^3)

B = moisture-dependency parameter (-).

The relationship between $DegT50_{matrix}$ and soil temperature is commonly described with the Arrhenius equation (e.g. EFSA, 2007b) and thus characterised by an Arrhenius activation energy:

$$DegT50_{matrix} = DegT50_{matrix,20Celsius}\exp\left(\frac{E_a}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]\right) \quad (2)$$

where

E_a = Arrhenius activation energy (kJ/mol)

R = gas constant (0.008314 kJ K^{-1} mol^{-1})

T = soil temperature (K)

T_{ref} = reference soil temperature (20°C = 293.15 K)

The relationship between $DegT50_{matrix}$ and soil depth is described by:

$$DegT50_{matrix} = \frac{DegT50_{matrix,topsoil}}{f_z} \quad (3)$$

where

$DegT50_{matrix,\ top\ soil}$ = $DegT50_{matrix}$ of the top 30 cm of soil

f_z = depth parameter (-).

FOCUS (2000) recommended using f_z = 1 for the layer 0-30 cm, f_z = 0.5 for the layer 30-60 cm, and f_z = 0.3 for the layer 60-100 cm.

It is commonly assumed that the effects of these three soil properties act independently of each other which results in:

$$DegT50_{matrix} = DegT50_{matrix,20Celsius,FC,topsoil} \left(\frac{\left(\frac{\theta}{\theta_{FC}} \right)^{-B}}{f_z} \exp\left(\frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right] \right) \right) \quad (4)$$

When analysing results of field dissipation studies, the inverse of Eqn 4 is more relevant:

$$DegT50_{matrix,20Celsius,FC,topsoil} = DegT50_{matrix} \; f_z \left(\frac{\theta}{\theta_{FC}} \right)^{B} \exp\left(\frac{E_a}{R} \left[\frac{1}{T_{ref}} - \frac{1}{T} \right] \right) \quad (5)$$

For scenario calculations with numerical models, the agreed convention is to specify this $DegT50_{matrix}$ of the top 30 cm of soil at a reference temperature of 20°C and a matric potential of pF = 2 (i.e. a matric suction of 100 hPa; see Koorevaar et al., 1983, for the background of matric potential) and to simulate the substance behaviour in soil based on default values for the relationships between on the one hand the $DegT50_{matrix}$ and on the other hand soil moisture, soil temperature and soil depth. Usually most of the plant protection product and of its soil metabolites will remain in the top 30 cm during the field dissipation study so the depth-dependency of the degradation rate is not considered to have an appreciable role. The moisture content and the temperature of the soil vary of course with time in field dissipation studies. Thus the $DegT50_{matrix}$ has to be calculated back via some inverse modelling procedure to the reference conditions 20°C and pF = 2. Only after this back calculation can the $DegT50_{matrix}$ be compared with $DegT50_{matrix}$ values from the laboratory studies at the same reference conditions. So the $DegT50_{matrix}$ derived from the field studies is not a direct measurement but may be 'contaminated' by a number of problems resulting from the inverse modelling procedure. The Panel identified several problems that undermine the soundness of this inverse modelling procedure:

(1) it is difficult to exclude loss due to photodegradation from the top millimetres with enough certainty based on current knowledge;

(2) the inverse modelling usually is based on default values for the parameter B and the E_a which may lead to large errors in estimated values of the $DegT50_{matrix}$ at 20°C and pF = 2;

(3) the numerical models commonly used in the inverse modelling procedure (e.g. PELMO and PEARL) have not been designed to simulate accurately temperature, moisture content and degradation rate in the top millimetres.

These problems are described in more detail in the following sections.

2.2. Difficulties with quantifying photodegradation and volatilisation losses at the soil surface

Photodegradation losses

The Panel considers current knowledge is insufficient to quantify photodegradation rates in the top millimetres of soil under the range of field conditions to be expected in the EU. OECD (2002a) developed a guideline for measuring soil photolysis in the laboratory. This study has become a standard data requirement for plant protection products. However, the Panel is not aware of studies in which photolysis rates measured under field conditions have been tested for a range of plant protection products and soils against predictions of numerical models based on measurements from this OECD guideline (see . This OECD study is commonly considered to be a 'route study' rather than a 'rate study', i.e. it is considered suitable for identifying photometabolites that are formed at the soil surface but it has not been designed to generate photodegradation rates that can be used to predict such rates under field conditions (EFSA, 2007b; p 9). The Panel recommends improving (i) the validation status of mechanistic models for simulating photodegradation rates at the soil surface and (ii) the methodology for measuring soil photolysis rates in the laboratory.

Light is efficiently absorbed by soil in a wavelength dependent manner (Tester and Morris, 1987). Sometimes it is argued in dossiers that absence of absorption of light from wavelengths from 295 to 800 nm (due to the lack of overlap of the sunlight emission spectrum with the absorption spectrum of the substance molecule) indicates that the substance will not be photodegraded on soil surfaces in the field. The absence of absorption of light indicates that direct photolysis of a substance does not occur. However, in surface water there is ample evidence for indirect photolysis. For instance, dissolved humic substances are efficient photosensitizers in surface waters (Miller and Chin, 2002). Also, in topsoil both in the solid and the liquid phase (i.e. in soil pore water), humic substances that can catalyse the photodegradation process may be present (Oliver, 2010; Katagi, 2004). The Panel considers therefore that indirect photolysis may also occur in the top millimetres of soil. So absence of light absorption cannot be used to exclude indirect photolysis.

As there is always sunlight in field studies, these considerations imply that photodegradation losses from the top millimetres can never be completely excluded on the basis of the properties of the molecule and laboratory studies on photodegradation available in the dossier.

Ciani et al. (2005) found that light penetrated no deeper than 0.2 mm into pellets consisting of a mixture of soils and barium sulphate. Soil photolysis studies with sieved soils indicated that direct and indirect photolysis is usually limited to the top 2 mm of soil (Hebert and Miller, 1990; Frank et al., 2002). These studies were done with soil surfaces that are prepared in the laboratory with sieved soil (mesh of 0.5 mm) as flat as possible (like a plane sheet). In field dissipation studies, the soil is usually rolled before application of the plant protection product (B. Gottesbüren, personal communication, 2010). Zhixiong et al. (2005) measured the surface roughness of a rolled Dutch loamy soil and found an average standard deviation of the surface height of 6 mm (the range was between 4 and 8 mm using measurements over lengths varying from 0.5 to 5 m and using different angles of measurement). Zobeck and Onstad (1987) reviewed rainfall and tillage effects on the so-called random roughness of the soil surface. This random roughness is defined as the standard error of individual soil elevations after oriented roughness has been removed. The lowest value of the random roughness in their review is about 5 mm (for a no-tillage system). A rolled soil surface is expected to give a low value of the surface roughness. So this minimum value is consistent with the measurement by Zhixiong et al. (2005). In view of this surface roughness of rolled soil it is not clear whether the photolysis will be limited to the top 2 mm of a rolled field soil and it will be difficult to define the level of the soil surface accurately at a millimetre scale.

Volatilisation losses

It would be helpful for the interpretation of field dissipation studies if volatilisation losses could be excluded on the basis of the properties of the substance. FOCUS (2008) proposed a trigger value of the vapour pressure of > 10^{-4} Pa (20°C) to check whether a substance has the potential to reach the air. However, Smit et al. (1997) collected volatilisation measurements from literature and they showed that measured volatilisation losses from soil are not well correlated to the saturated vapour pressure. Instead, these are better correlated to the fraction of the pesticide calculated to be present in the gas phase. For the evaluation of field dissipation studies, it is sufficient that the volatilisation loss is less than about 5%. Data from Smit et al. (1997) indicate that this requirement is met if the fraction in the gas phase is less than about 10^{-8}. The criteria from FOCUS (2008) and Smit et al. (1997) are based on different properties of the soil-substance system. So for part of the substance-soil systems the vapour pressure may be below 10^{-4} Pa (20°C) whereas the fraction in the gas phase is higher than 10^{-8}. Simulations with numerical models cannot solve this problem as they are at the moment insufficiently accurate for low volatile substances (Ferrari et al., 2003). The Panel recommends improving the validation status of mechanistic models for simulating volatilisation of spray applications at the soil surface.

2.3. Uncertainties resulting from the use of default values of B and E_a

The inverse modelling procedure uses default values of B for the moisture dependency relationship and of E_a for the temperature relationship. Let us first consider B. FOCUS (2000) recommends using a default B value of 0.7 based on Gottesbüren (1991). However, Gottesbüren (1991) reported 94 B values and these show considerable variability (minimum of 0.03 and maximum of 2.9); ten of these 94 are above 1.5. Figure 3 shows that a B value of 1.5 in air-dry soil (θ/θ_{FC} of 0.05 to 0.1) will lead to a $DegT50_{matrix}$ that is six to eleven times longer than the default B value of 0.7. So when an inversely modelled $DegT50_{matrix}$ would have been mainly based on the decline in dry soil for a system with a true B value of 1.5, this would lead to a $DegT50_{matrix,FC}$ that is much too long as follows from the following example calculation:

(i) observed $DegT50_{matrix}$ = 50 d in field

(ii) actual θ / θ_{FC} in field of 0.1

(iii) inversely modelled $DegT50_{matrix,FC}$ = 2 d, based on true B of 1.5 using Eqn 5

(iv) inversely modelled $DegT50_{matrix,FC}$ = 10 d, based on assumed B of 0.7 using Eqn 5.

The opposite (i.e. an inversely modelled $DegT50_{matrix,FC}$ that is too short) may of course also occur. This happens if the true B value is close to zero (see line for B = 0.1 in Figure 3). It may also happen if the $DegT50_{matrix}$ does not decrease continuously with decreasing moisture content as in most studies (see Smelt et al., 1979, for an exceptional example with a $DegT50_{matrix}$ of oxamyl in air-dry soil that was even shorter than the $DegT50_{matrix}$ at a moisture content of 0.2 kg/kg).

A conservative approach is not to simulate θ but to assume that it is continuously at field capacity (this approach is regularly used in regulatory exposure assessments). Then the value of B does not matter (see Eqn 1). However, it should be kept in mind that such an approach may generate an upper limit of the $DegT50_{matrix,FC}$ when using the resulting $DegT50_{matrix,FC}$ further in the exposure assessment (see Section 5.2).

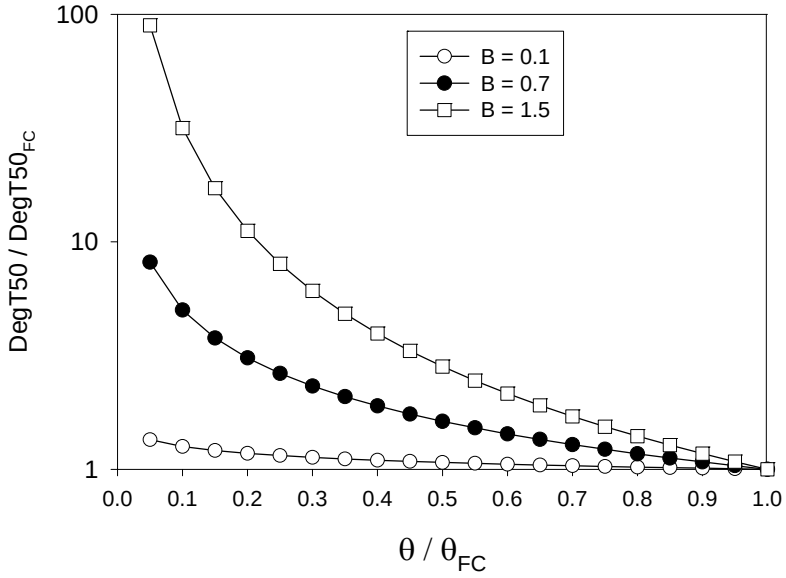

Figure 3: The ratio $DegT50_{matrix}$ / $DegT50_{matrix,FC}$ as a function of the ratio $\theta/\ \theta_{FC}$ for different B values as calculated with Eqn 1.

EFSA (2007b) showed that the E_a value of 99 individual substance-soil combinations varied considerably: 95% of the values were in the range from about 35 to 115 kJ/mol. So use of the default E_a of 65 kJ/mol may lead to a considerable uncertainty in the inversely modelled $DegT50_{matrix}$ at 20°C. Let us consider as an example a field study with an average soil temperature of 14°C that resulted in a $DegT50_{matrix}$ of 100 days. Eqn 5 gives then an inversely modelled $DegT50_{matrix,20Celsius}$ of 68 d for E_a = 65 kJ/mol but for E_a = 35 kJ/mol the inversely modelled value is 81 d and for E_a = 115 kJ/mol it is 51 d. So for true E_a values that are higher than the 65-kJ/mol default value, the inverse modelling procedure using the default value will give a $DegT50_{matrix,20Celsius}$ value that is too long and for true E_a values that are lower than the 65-kJ/mol the inversely modelled $DegT50_{matrix,20Celsius}$ will be too short.

Table 1 summarizes the effects of the use of default values of in B and E_a as described above and considers also the net effect on the transformation rate as simulated in exposure scenarios. This net effect is expected to be zero because the same default values are used in the exposure calculations for the required exposure scenario. For example, if a field dissipation study is carried out at an average soil temperature of 10°C, about the same half-life will be calculated in the required exposure scenario at 10°C irrespective of the value of the E_a because the errors cancel out. This cancelling out is expected to occur for large numbers of scenarios and substances. However, when using $DegT50_{matrix}$ values from field studies in the risk assessment of an individual plant protection product (which is the case to be considered), these default values lead to additional uncertainty.

2.4. Weaknesses of the numerical models for describing moisture and temperature fluctuations and degradation rates in the top millimetres of soil

Numerical models such as PELMO and PEARL assume a potential evaporation rate that is constant over a day. However, measurements by Jackson (1973) showed that there may be a strong daily course in the moisture content of the top millimetres resulting from the daily variation in this evaporation rate (Figure 4). Thus modelling soil moisture dynamics in the top few millimetres is a daunting task. Diurnal surface soil moisture dynamics depends on processes like evaporation, condensation (dew), liquid flow in capillary pores and films and vapour diffusion in air-filled pores. Despite the fact that not all of these processes are included in currently used soil water flow models that are used for

pesticide fate modelling in soils, these processes also depend strongly on soil properties and soil structures which change dynamically over time (due to compaction by rain, loosening by wetting-drying cycles, thawing-freezing cycles).

The numerical models usually use numerical compartment thicknesses in the top soil of about 2.5 cm (FOCUS, 2000). This is another reason for inaccurate simulation of soil moisture contents in the top millimetres: e.g. measurements by Jackson (1973) showed considerable differences in measured moisture contents between the 0-5 mm and 5-10 mm layers during the drying process. The Panel expects that the numerical models in general will overestimate the soil moisture content of the top millimetres during a drying cycle in the field because of the constant potential evaporation rate and the 2.5-cm thick compartments. Such an overestimation will lead to inversely modelled values of the $DegT50_{matrix}$ at 20°C and pF = 2 that are too long. This is illustrated with the following example in which it is assumed that the total areic[7] mass of plant protection product is present in the top 5 mm of soil at a constant volume fraction of water:

(i) observed $DegT50$ = 50 d in field

(ii) actual θ = 0.05, simulated θ = 0.10, θ_{FC} = 0.2

(iii) inversely modelled $DegT50$ = 19 d based on actual θ using Eqn 5 with B = 0.7

(iv) inversely modelled $DegT50$ = 31 d based on simulated θ using Eqn 5 with B = 0.7.

However, when performing scenario calculations, the net effect on the exposure assessment is expected to be zero because in the scenario calculations the moisture content is also overestimated.

[7] 'Areic mass' means mass per area (Rigg et al., 1985).

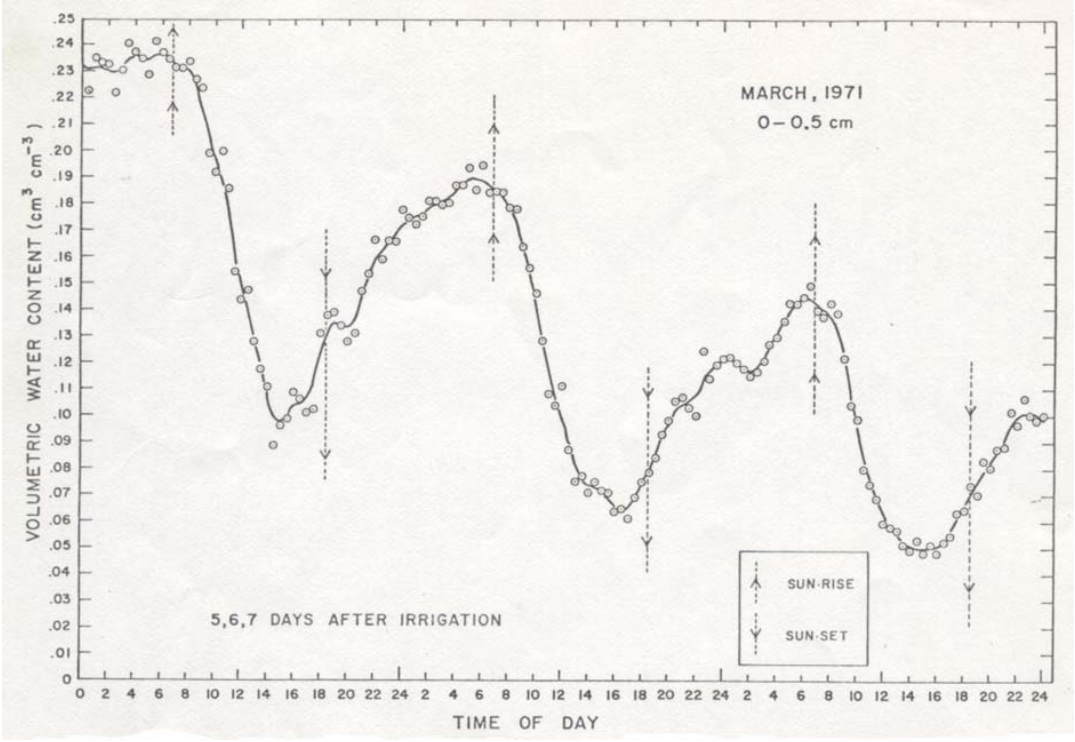

Figure 4: Measured soil water content in the top 5 mm of bare Adelanto loam soil as a function of time on 7-9 March 1971 in Phoenix (Arizona) after 100 mm of irrigation on 2 March (taken from Jackson, 1973). Daily maximum air temperatures ranged from 17 to 24°C and daily minimum air temperatures from -2 to 5°C.

The numerical models use daily average air temperature as input and the effect of solar radiation on the soil temperature is ignored (FOCUS, 2000). This has been shown to work well for simulation of daily averages of soil temperatures at 5 cm depth (e.g. Scorza Junior and Boesten, 2005). However it is unlikely that this works well for daily fluctuations in the top millimetres because solar radiation will have a considerable effect in these top millimetres and because also air temperatures may fluctuate considerably during the course of the day. The inadequacy of the numerical models to describe the moisture content in the top millimetres combined with ignoring solar radiation and using daily average air temperatures will therefore predictably lead to poor description of the daily course of soil temperature in the top millimetres. This can be illustrated by measurements by Steenpass et al. (2010) (Figure 6). These show daily fluctuations of the soil surface temperature of about 15 to 22 °C in September in Jülich (Germany) which is at about 51° Northern Latitude. One may expect that daily fluctuations of soil surface temperatures at more southern European latitudes in spring and summer are considerably higher than those measured in Jülich. This was confirmed by Braud et al (1993), who measured daily fluctuations of temperature at 1 cm depth of a bare silt loam soil from 20 June to 1 July 1991 in Spain. They found that this temperature fluctuated typically between 17 and 50°C and on one day even from 15 to 55°C. So these are daily fluctuations of 33 to 40°C at 1 cm depth. To further test the expectation of larger daily fluctuations in southern Europe, the Panel calculated the average difference between daily maximum and minimum air temperatures for the nine FOCUS groundwater scenarios (FOCUS, 2000). This is based on a time series of 20 years. These daily fluctuations are indeed higher for the more southern scenarios (Figure 5), the only outlier in this trend being the Porto scenario at 41° Northern Latitude which is close to the Atlantic Ocean. Such findings are only indirect evidence for this trend because the temperature fluctuations in soil may differ from those in air.

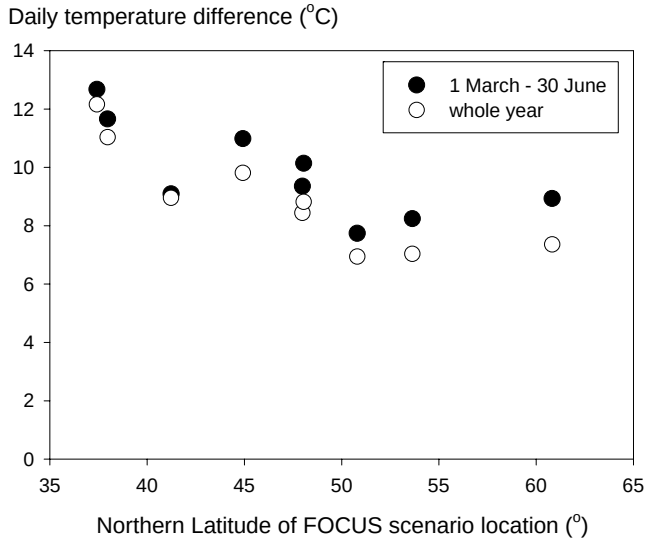

Figure 5: Average daily difference between minimum and maximum air temperature (averaged over 20 years) as a function of the Northern Latitude for the nine FOCUS groundwater scenarios taken from FOCUS (2000). The two symbols indicate the differences for (i) the whole calendar year and (ii) the period from 1 March to 30 June.

Steenpass et al. (2010) measured also soil temperatures at 3 and 6 cm depth in this soil and found daily fluctuations (i.e. differences between daily minimum and maximum temperatures) of about 14 °C at 3 cm and 11 °C at 6 cm (as compared fluctuations of 15-22°C at the soil surface). Thus the daily fluctuations in soil temperature decrease only moderately with depth in the top centimetres and also that the daily fluctuations at a few decimetres depth are probably much smaller than those in the top centimetres.

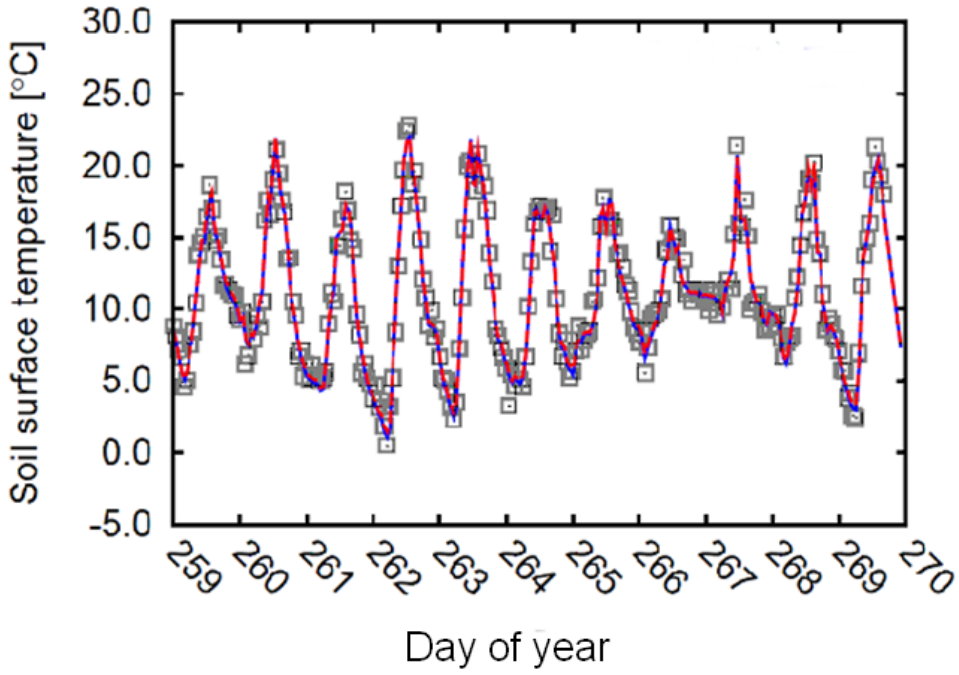

Figure 6: Soil-surface temperature measured from 15 to 26 September 2008 at an experimental field close to Jülich (Germany). The soil was bare and its texture was silt loam. The points are the measurements and the line is a calculated with a simulation model (taken from Steenpass et al., 2010).

Let us assume that the Arrhenius equation gives a reliable description of the relationship between the $DegT50_{matrix}$ and soil temperature in the top millimetres. Let us furthermore consider the following example: (i) a substance with a $DegT50_{matrix}$ of 60 days at 20°C and an Arrhenius activation energy of 65 kJ/mol, (ii) soil temperature fluctuates on a daily basis sinusoidally around an average temperature of 20°C. Figure 7 shows that introducing a fluctuating temperature in this example calculation speeds up the simulated decline. The simulated time points were fitted to a first-order decline and this resulted in half-lives of 60 days for constant temperature, 50 days for an amplitude of 10 °C and 32 days for an amplitude of 20°C. So an amplitude of 20°C speeds up the degradation rate by about a factor of two. One might argue that this effect of the daily temperature fluctuations is consistently included in the exposure assessment: the fluctuations are both ignored in the inverse modelling procedure and in the scenario calculations with the numerical models. However, the effect of these fluctuations is expected to be considerably larger in Southern Europe than in Northern Europe. So the use of $DegT50_{matrix}$ values derived from field studies in Southern Europe for exposure assessments in Northern Europe may lead to overestimation of the transformation rate in Northern Europe and vice-versa (Table 1).

In the calculations for the FOCUS groundwater scenarios (FOCUS, 2000), the $DegT50_{matrix}$ is extrapolated up to 100 cm depth via the unique f_z relationship (Eqn 3). One may expect that daily fluctuations in soil temperature decrease strongly with depth between 0 and 100 cm. The $DegT50_{matrix}$ will in most of the field studies mainly be based on the measured decline in the top centimetres (also because usually unweighted fitting procedures are used as recommended by FOCUS, 2006). In the leaching calculations, this $DegT50_{matrix}$ is also used to calculate the degradation rate in deeper layers in which daily temperature fluctuations are much smaller (note that in the simulations, daily fluctuations are not considered at all). So this may lead to overestimation of the transformation rate in the deeper layers and thus to systematic underestimation of the leaching concentrations in the FOCUS groundwater scenarios when using $DegT50_{matrix}$ values derived from field studies. These are potential

effects based on the assumption that the Arrhenius equation is correct at a time scale of hours. The Panel is not aware of evidence for or against this assumption for PPPs but it is known that soil respiration varies over this time scale (Parkin and Kaspar, 2004).

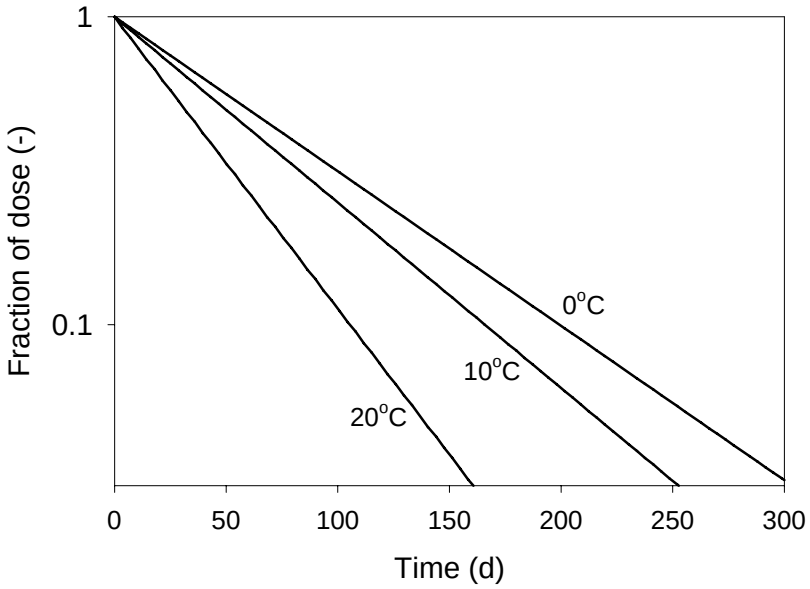

Figure 7: Effect of the daily amplitude of soil temperature on calculated decline of substance in a closed laboratory soil system assuming first-order degradation kinetics and using the Arrhenius equation to describe the effect of temperature on the degradation rate coefficient. The *DegT50* at 20°C was 60 d and the Arrhenius activation energy was 65 kJ/mol. Calculations were made for an average soil temperature of 20°C and a daily sinusoidally fluctuating soil temperature with amplitudes of 0, 10 and 20 °C; amplitude is defined as the difference between the maximum (or minimum) and the mean of the sinus.

Similarly there is no evidence that the relationship between $DegT50_{matrix}$ and the soil moisture content of Eqn 1 works well at a time scale of hours for changing courses of moisture content with time as shown in Figure 4. Let us assume that Eqn 1 gives a reliable description of the relationship between the $DegT50_{matrix}$ and the volume fraction of water, θ, in the top millimetres. Let us furthermore consider the following example: (i) a substance with a $DegT50_{matrix}$ of 60 days at a θ of 0.2 (field capacity) 20°C and a B value of 0.7, (ii) θ fluctuates on a daily basis sinusoidally around an average θ of 0.1. Figure 8 shows that introducing a fluctuating θ in this example calculation slowed down the degradation rate slightly. However, this problem may be overcome by ignoring the effect of soil moisture in the inverse modelling procedure which leads to a conservative $DegT50_{matrix}$.

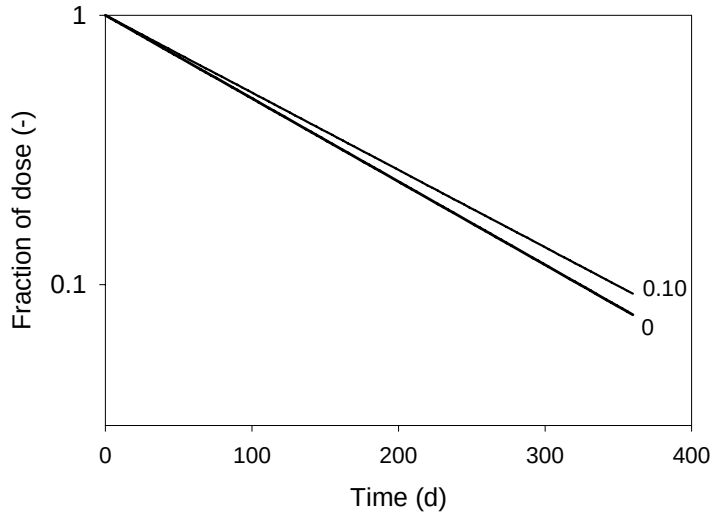

Figure 8: Effect of the daily amplitude of volume fraction of water in soil on calculated decline of substance in a closed laboratory soil system assuming first-order degradation kinetics and using Eqn 1 to describe the effect of the volume fraction of water on the degradation rate coefficient. The *DegT50* at θ = 0.2 was 60 d and the exponent B was 0.7. Calculations were made for a daily sinusoidally fluctuating volume fraction of water with amplitudes of 0 and 0.10 around an average volume fraction of water of 0.10; amplitude is defined as the difference between the maximum (or minimum) and the mean of the sinus.

Table 1: Overview of effects when estimating *DegT50* values from field studies and their consequences for these values and for the transformation rate in exposure scenario calculations.

Problem	***Effect on value of inversely modelled DegT50 for top soil at 20°C and pF = 2***	***Effect on transformation rate of a parent plant protection product in exposure scenario calculations: overestimation or underestimation of rate?***
Use of default value of 0.7 for *B* parameter describing the moisture dependency of the degradation rate	Random error in *DegT50*: too short if B< 0.7 and too long if B > 0.7	Net effect is expected to be zero when considering many scenarios and substances; for individual scenarios and substances, this problem leads to random uncertainty
Use of default value of 65 kJ/mol for E_A parameter describing the temperature dependency of the degradation rate	Random error in *DegT50*: too short if E_A < 65 kJ/mol and too long if E_A > 65 kJ/mol	Net effect is expected to be zero when considering many scenarios and substances; for individual scenarios and substances, this problem leads to random uncertainty
The calculated moisture content in top millimetres is systematically too high	Systematic overestimation of *DegT50* (based on Eqn 5)	Net effect is expected to be zero when considering many scenarios and substances because the moisture content is too high also in the scenario calculations; for individual scenarios and substances, this problem leads to random uncertainty

Systematic underestimation of daily fluctuations of moisture content	Systematic slight overestimation of *DegT50* because decline with fluctuating moisture is slower than with constant moisture (see Fig. 7)	Net effect is expected to be zero when considering many scenarios and substances because the fluctuations are also ignored in the scenario calculations
Systematic underestimation of daily fluctuations in calculated soil temperature for the top millimetres	Systematic underestimation of *DegT50* because decline with fluctuating temperature is faster than with constant temperature (see Fig. 6)	For soil exposure assessment, net effect is expected to be zero when considering many scenarios and substances because the fluctuations are also ignored in the scenario calculations; for northern scenarios, possibly a net overestimate of the rate because the fluctuations are less than average and for southern scenarios possibly a net underestimate of the rate; for all leaching scenarios, possibly a net overestimate of the rate (so underestimation of leaching) because the amplitude of the daily temperature fluctuations decreases strongly with depth in the top metre of the soil profile

2.5. Concluding remarks on the problem and proposed solution

The problems described in the preceding sections fall into two categories:

A. the difficulties in completely excluding a competing loss process from the top millimetres

B. the difficulties of obtaining a reliable DegT50matrix at 20oC and pF = 2 from measured declines in the top millimetres via the described inverse modelling procedure.

These two problem categories are independent of each other. Both problem categories are difficult to solve and will require considerable research efforts. If problem A is ignored, this will lead to a too short DegT50matrix and also to an underestimate of the concentrations in the exposure assessments (considering parent molecules only). The direction of the error in the DegT50matrix resulting from problem B is variable: the DegT50matrix may be either too short or too long. The resulting effect on the exposure assessment is mostly variable; only the effect of the temperature fluctuations on the leaching concentrations has probably a clear direction (i.e. systematic underestimation of leaching concentrations (Table 1). It is in general undesirable that a higher-tier estimation of a model input parameter such as the DegT50matrix is not very reliable. However, this lack of reliability has to be balanced against the advantage that field dissipation studies are closer to the reality to be assessed than are laboratory incubations. For persistent compounds especially, the laboratory incubations may generate too long DegT50matrix values.

The Panel proposes to base this guidance proposal on the assumption that an inversely modelled $DegT50_{matrix}$ at 20°C and pF = 2 needs to be based on a measured decline that took place below the top millimetres of the soil. So the experimental period of a field dissipation study has to be split into two parts: in the first part the bulk of the substance is still in the top millimetres and in the second part this bulk has moved to lower depths.

The Panel proposes to split the field dissipation study into two parts based on the following procedure: (i) fit the normalised decline curve to a biphasic decline model, and (ii) accept the rate coefficient of the slow phase of this biphasic decline only if at the transition between the two phases at least 10 mm of rain (approximately equivalent to a week's rainfall in many parts of the EU) has fallen since

application of the plant protection product. This rainfall criterion is added to ensure that the slow phase of the biphasic decline does not represent a second initial loss process; e.g. first very rapid indirect photolysis followed by volatilisation without any rain falling onto the field. The Panel considers the probability of occurrence of two significant competing surface loss processes to be low so this rainfall criterion does not play an important role. Should there be no significant biphasic trend in the decline (SFO-type decline curves), the proposed solution is still to ignore the data points until the 10 mm of rain has fallen (further details in the next chapter). It is accepted that this 10-mm criterion is a pragmatic and simple solution to a complicated problem, and it has the merit also of eliminating the scatter often observed in the first few sampling points.

The Panel has considered the possibility of proposing a criterion based on the properties of the substance (requiring for example that at least 90% of the remaining amount should have penetrated beyond 2-5 mm depth). Such a requirement would lead to a rainfall criterion that depends on the K_{om} and the water solubility of the substance. However, available models such as PELMO and PEARL have not been designed for such shallow penetration depths: e.g. their description of the dispersion of solutes in the top millimetres is probably inadequate and they do not consider the limiting effect of water solubility which may be relevant for compounds such as simazine (Nicholls et al., 1984).

A study by Erzgräber et al. (2009) shows that 10 mm may not be enough to exclude surface loss processes under all circumstances; for a strongly sorbing substance that showed rapid indirect photolysis in soil in twelve field studies, decline curves with a biphasic model showed that cumulative rainfall was on average about 30 mm (with range from about 10 to 90 mm) when the slow phase started.

The consequence of the fixed 10-mm criterion is that there will be occasionally unjustified rejection of a few early data points of a decline curve for compounds with low K_{om} and occasionally unjustified acceptance of a few early data points for compounds with high K_{om} or low water solubility.

3. Proposed guidance for analysing results of field dissipation studies

3.1. Introduction

Field dissipation studies are commonly carried out by spraying a plant protection product onto bare soil, with usually a crop then being grown. The decline of the soil residues with time is measured by regular soil sampling often to 50 or 100 cm depth. The guidance proposal in this chapter is restricted to studies with spraying onto bare soil; studies with spraying onto a crop are discussed in Chapter 4.

This guidance proposal is restricted to studies in which plant uptake did not contribute significantly to the dissipation of the plant protection product. The simplifying assumption is made that any additional dissipation processes due to the presence of weeds or crops does not have an appreciable impact on the estimated loss rates from soil; there is substantial evidence to support this assumption. Firstly, modelling of such uptake (Trapp and Mc Farlane, 1995), although extremely complex due to the need to match the distribution of roots, water and pesticide, does not predict substantial amounts of uptake. The roots are always a small compartment compared to the soil itself. Furthermore, those pesticides well transported to shoots from soil (i.e. having a high TSCF) require a log K_{ow} (octanol-water partition coefficient) of 0.5 to 1.0; such non-ionised compounds are thus weakly sorbed by soil and so potentially leachable, and so in practice could not be registered unless they had a short half-life in soil which thereby limits the opportunity for uptake by plants. A second approach is to consider the findings of field studies in which pesticide dissipation has been measured on plots with and without crops. For example, the loss of five persistent triazole fungicides (log K_{ow} 2.3 to 3.72) was measured at two sites on plots with bare soil (surface applied or shallowly incorporated) or applied to a young wheat crop (Bromilow et al., 1999). After one year, the concentrations in soil were similar for each compound irrespective of the presence or absence of plants; it is thought that the extra dryness in the cropped plots might have slowed degradation in soil and so offset the small amount of uptake by the wheat. This simplifying approach is of course conservative, and would not automatically preclude scenarios in which weeds or crops were present.

This guidance proposal is intended to be used for studies in which most of the remaining amount is present in the top 30 cm depth. The background is that the Panel considers studies with significant leaching below 30 cm depth not suitable for estimating a $DegT50_{matrix}$ for the top layer in view of the additional uncertainty in the inverse modelling procedure in PELMO and PEARL resulting from uncertainty in the depth factor f_z (Eqn 5).

The aims of the guidance proposal in this chapter are the following subset of the general aims described in Section 1.2:

(i) to develop procedures for estimating $DegT50_{matrix}$ values reliably from results of individual field dissipation studies

(ii) to develop procedures for estimating top-soil decline parameters reliably from results of individual field dissipation studies.

3.2. Estimation of model input parameters using normalised decline curves

Introduction

In the past five years, the time-step normalisation procedure as described by FOCUS (2006; p. 179) has become popular in the EU registration. This procedure assumes that the decline in the field can be described well by numerical models that assume first-order degradation kinetics such as PELMO, PRZM and PEARL (see Appendix 8 of FOCUS, 2006, for details). The procedure implies that the decline curve after normalisation can be used directly to estimate the $DegT50_{matrix}$ of the top soil at

20°C and pF = 2. As described before, the Panel considers such an estimate only acceptable if measures are taken to ensure that the $DegT50_{matrix}$ does not include surface loss processes.

The proposal is structured as follows. First an overview is given of the candidate models that might be used to describe the decline curve and the most suitable models are selected. Stepped approaches are then proposed for these models to derive the appropriate endpoints from each field dissipation study.

Selection of models for describing bi-phasic kinetics

As follows from the preceding considerations, the procedure has to consider the possibility that the dissipation rate in field dissipation studies is faster in the initial stage of the study than subsequently. Such dissipation patterns cannot be described adequately with single first-order kinetics. Instead models describing biphasic kinetics are to be preferred. FOCUS (2006) recommended three models for describing bi-phasic kinetics: the bi-exponential model, the Gustafson-Holden model and the hockey-stick model.

The bi-exponential model (hereafter called the DFOP model from 'Double First-Order in Parallel') is based on the assumption that a mass of plant protection product is present in two non-interacting compartments in the system and in which the product may be degraded at differing rates assuming first-order kinetics. This results in the following expression of the time course of the mass *m* in the system:

$$m = m_{ini,fast}\ \exp(-k_{fast}\, t) + m_{ini,slow}\ \exp(-k_{slow}\, t) \qquad (6)$$

where
$m_{ini,fast}$ = mass in system in the fast-degrading compartment at the start (kg)
$m_{ini,slow}$ = mass in system in the slow-degrading compartment at the start (kg)
k_{fast} = rate coefficient in the fast-degrading compartment (d^{-1})
k_{slow} = rate coefficient in the slow-degrading compartment (d^{-1})
t = time (d).

The qualifications 'slow' and 'fast' have no absolute meaning in this context: the highest rate coefficient of the two is by definition the fast one and the other is thus the slow one.

Eqn 6 can be rewritten as:

$$m = m_{ini}\left(g\ \exp(-k_{fast}\, t) + \left(1-g\right)\ \exp(-k_{slow}\, t)\right) \qquad (7)$$

where
m_{ini} = total mass in the system at the start (kg)
g = fraction of total mass in the system applied to the fast-degrading compartment (-)

The use of the DFOP model leads to a breakpoint time (t_b), defined as the moment where the degradation of the fast decay is replaced by the slow decay; determination of the breakpoint time is not however straightforward because the slope of the DFOP decreases gradually. The Panel proposes defining the breakpoint time as:

$$t_b = \frac{3 \ln 2}{k_{fast}} \qquad (8)$$

when 87.5 % of the fast-degrading compartment has disappeared.

The Gustafson-Holden model (hereafter called the FOMC model from 'First-Order Multi-Compartment'; FOCUS, 2006) is based on the assumptions that there are an infinite number of non-interacting compartments which each degrade at their own rate (assuming first-order kinetics) and that the frequency distribution of the rate coefficients of these compartments can be described by a gamma function. This gives the following equation for the FOMC model:

$$m = \frac{m_{ini}}{\left(\frac{t}{\beta}+1\right)^{\alpha}} \tag{9}$$

where
α = so-called shape parameter (-)
β = so-called location parameter (d)

The Hockey-Stick model (hereafter called the HS model) is based on the assumption that the mass in the system declines according to first-order kinetics but at a certain point in time ('the breakpoint') the rate coefficient changes:

$$\begin{aligned} t \le t_b \quad & m = m_{ini}\exp(-k_1 t) \\ t > t_b \quad & m = m_{ini}\exp(-k_1 t_b)\,\exp(-k_2\,(t-t_b)) \end{aligned} \tag{10}$$

where
t_b = breakpoint time (d)
k_1 = rate coefficient until t_b (d^{-1})
k_2 = rate coefficient after t_b (d^{-1})

Our aim is to describe a normalised decline of the areic mass of a plant protection product in soil of a field dissipation study. This decline is expected to show a rapid initial phase in the period when surface loss processes play an important role followed by a slower phase that is dominated by the degradation rate within the soil matrix. It is also possible that the normalised decline shows a slow initial phase followed by a faster decline later. The purpose of this proposal is to use the decline in the second phase to derive a normalised $DegT50_{matrix}$ as input to models such as PRZM, PELMO and PEARL. These models are based on first-order kinetics and also the time-step normalisation procedure is based on the assumption of first-order kinetics. Thus the Panel considers the FOMC model not suitable because it does not describe a first-order decline in the second phase.

So the remaining options are the DFOP and HS models. The Panel recommends considering both models for deriving a normalised $DegT50_{matrix}$. The DFOP model has the advantage that it describes a gradual transition between the two phases but the disadvantage that it can only describe a decline that is faster at the start than at the end. The HS model has the advantage that it can describe both a decline that is faster at the start than at the end and a decline that is slower at the start than at the end. However it has the disadvantage that there is an abrupt transition between the two phases.

Stepped approach for evaluating normalised decline curves with the DFOP or Hockey-Stick models

The Panel proposes the flow charts (Figures 8 and 9) for evaluating normalised decline curves. Box 1 in Figure 9 checks whether the decline in laboratory studies shows a lag-phase or a slowing down of the decline due to long-term sorption kinetics. Such cases will not occur often but, if it happens, the recommendation is to use expert judgement based on the restriction that the data points before 10 mm rain has fallen should not influence the estimation of the $DegT50_{matrix}$ (Box 2). The next step (Box 3) is to check whether the normalised field decline curve can be described well with SFO kinetics using procedures proposed by FOCUS (2006). If yes, then go to box 4: eliminate the data points before 10 mm of cumulative rainfall and fit SFO to the remainder of the points to get the $DegT50_{matrix}$. If no, then fit DFOP and estimate the breakpoint time (Equation 8, Box 5).

The breakpoint time corresponds with a time equal to three half-lives of the fast-degrading compartment, so $g \exp(-k_{fast}\ t_b) = 0.125\ g$. This implies that, at this breakpoint time, 87.5% of the decline of the fast-degrading compartment has taken place. Therefore it is likely that after this breakpoint time, the slow-degrading compartment dominates the overall decline. Only for high g values may this not be the case. For example, if $g = 0.9$ then $0.125\ g = 0.11$ whereas $(1 - g)$ may still be close to 0.1. In such a case the breakpoint time estimated with Eqn 10 may be too short. Therefore it is checked in Box 6 whether g is below 0.75; if no, the Panel recommends going to the HS flow chart (Figure 10) because the estimate of the breakpoint time with Eqn 10 is not reliable enough.

Box 7 checks whether the rate coefficients k_{fast} and k_{slow} are significantly different. This is considered necessary because the breakpoint time will be quite uncertain if this is not the case. If they are significantly different, Box 8 tests whether the cumulative rain is at least 10 mm at the breakpoint time (please note that normalised time and true time are different and the rainfall should of course be linked to the true time). If this is not the case, k_{slow} has to be rejected because it is too strongly influenced by processes in the top millimetres. In such a case, go to the Hockey-Stick flow chart because this has an iteration option to use the data after modification. If cumulative rain was at least 10 mm at the breakpoint, Box 9 is reached. The problem considered here is that k_{slow} may be not accurate enough, for example because it is based on only a few data points or because the data show considerable scatter. The Panel recommends testing this accuracy by following procedures similar to those recommended by FOCUS (2006). If k_{slow} is accurate enough, the bottom box of the flow chart is reached and k_{slow} can be used. If not, the option is offered to go to the HS flow chart.

If the flow chart in Figure 9 results in a useful k_{slow} ,then the resulting $DegT50_{matrix}$ can be calculated as ln 2/ k_{slow} and the rapidly dissipating fraction F_{field} can be calculated from the difference between the initial areic mass A_0 and the areic mass at the breakpoint time t_b (A_{Tb}) according to the following equation:

$$F_{field} = \frac{A_0 - A_{Tb}}{A_0} \tag{11}$$

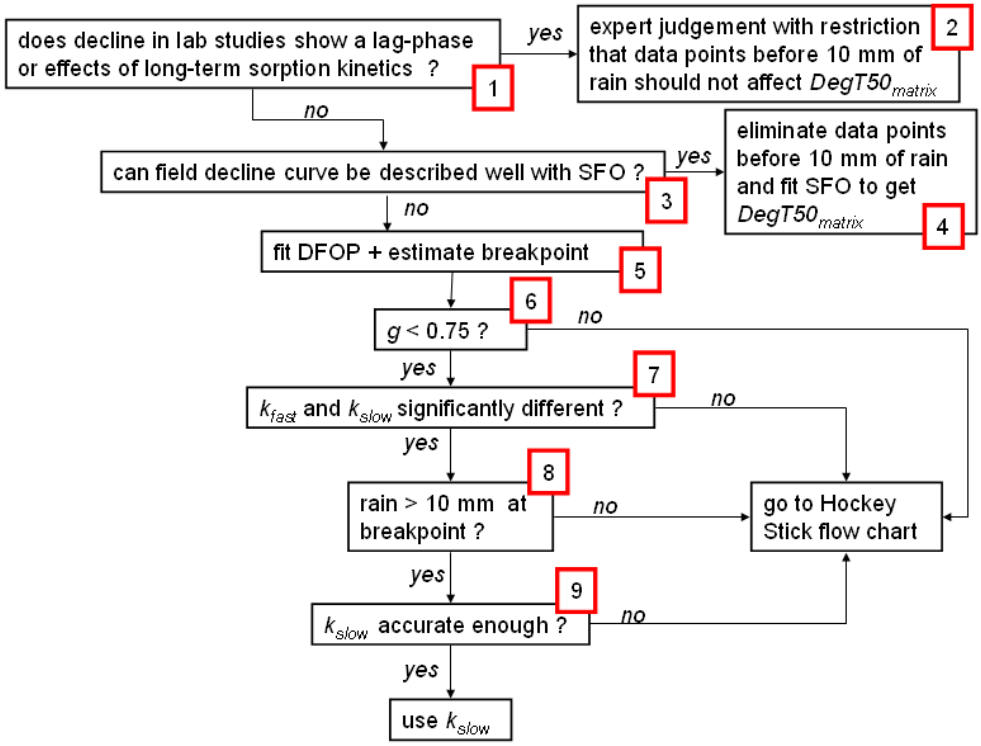

Figure 9: Flow chart for assessment of results of field dissipation studies after analysis with the DFOP model. The numbers 1 to 9 act as references to the corresponding boxes in the main text. The test of the accuracy in box 9 should be done by following procedures similar to those recommended by FOCUS (2006).

The proposal for evaluating results of field dissipation studies with the HS model is based on the flow chart (Figure 10). The first step is:
i. transform the measured time series of remaining amounts into a normalised time series using the time-step normalisation approach described by FOCUS (2006; p. 179)
ii. fit the normalised time series to the HS model as described by FOCUS (2006).

Next it is tested (Box 1, Figure 10) whether the cumulative rain is at least 10 mm at the breakpoint time (please note that normalised time and true time are different and the rainfall should of course be linked to the true time). If this is not the case, k_2 has to be rejected because it is too strongly influenced by processes in the top millimetres. However, Box 3 offers the option to fix the breakpoint at the time when 10 mm of rain has fallen and to refit k_2 .

If cumulative rain was at least 10 mm at the breakpoint, Box 2 is reached. The problem considered here is that k_2 may be not accurate enough because it is based on only a few data points or because the data show considerable scatter. The Panel recommends testing this accuracy following procedures similar to those recommended by FOCUS (2006). If k_2 is accurate enough, Box 4 tests whether $k_1 > k_2$. If this is indeed the case, k_2 can be accepted. If not, there is the possibility that after some time accelerated degradation occurred in the field study which may happen in some soils but not in others. So then the resulting k_2 is not representative enough in which case this field study should not be used.

If the flow chart in Figure 10 results in a useful k_2, then the resulting $DegT50_{matrix}$ can be calculated as ln 2/ k_2. It is only meaningful to calculate the rapidly dissipating fraction F_{field} if $k_1 > k_2$. If this is the case, F_{field} can be calculated on the basis of the difference between the initial areic mass and the areic mass at the breakpoint time t_b.

As follows from the guidance above, the values of k_{fast} and k_1 are not further used in the exposure assessment. These values should also not be considered reliable because the normalisation process considers only the effect of soil temperature and soil moisture on the degradation rate within the soil matrix which has no meaning for surface losses due to indirect photolysis or volatilisation.

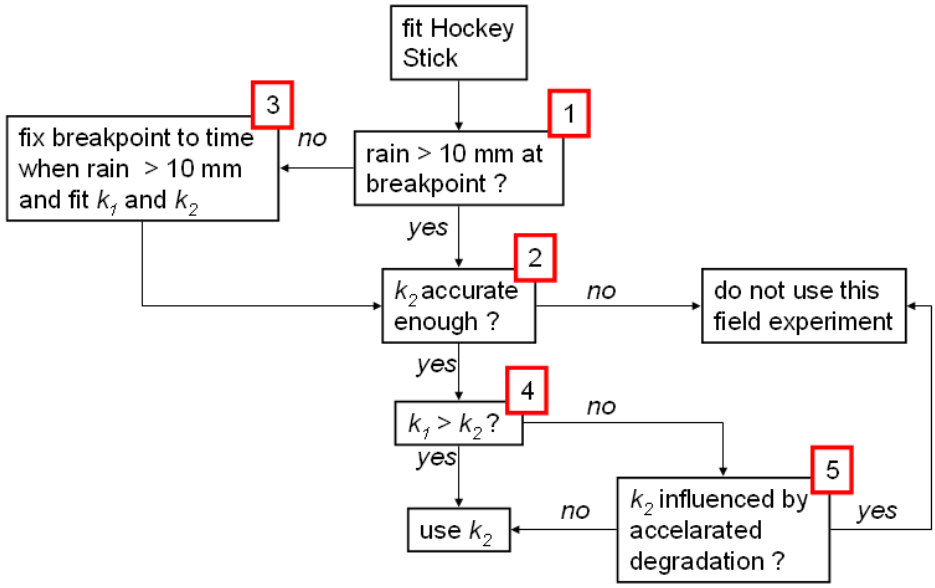

Figure 10: Flow chart for assessment of results of field dissipation studies after analysis with the Hockey-Stick model. The numbers 1 to 5 act as references to the corresponding boxes in the main text. The test of the accuracy in box 4 should be done by following procedures similar to those recommended by FOCUS (2006).

The $DegT50_{matrix}$ values estimated using the flow charts of Figures 9 and 10 should be interpreted with consideration of existing information in the dossier on the potential for volatilisation and indirect photolysis (Section 2.2.) and the degradation rates from the laboratory soil tests. The Panel recommends checking whether any of the individual $DegT50_{matrix}$ values is significantly longer (t-test at 5% level as described in Appendix A) than the laboratory *DegT50* values. In general, $DegT50_{matrix}$ values from field studies are expected to be shorter than *DegT50* values from laboratory studies but the opposite may happen occasionally (Beulke et al., 2000). The Panel considers it very unlikely that a laboratory study with a certain soil shows systematically and consistently a faster degradation rate than a field study with the same soil at the same temperature and moisture content. The Panel considers it far more likely that a field $DegT50_{matrix}$ that is significantly longer than the geomean laboratory *DegT50* is caused by systematic errors in the inverse modelling procedure (e.g. B or E_a values of this substance-soil combination that differ strongly from the assumed default values or poor simulation of soil temperature or soil moisture in soil). It can of course also happen by coincidence because the number of measured laboratory and field *DegT50* values may be limited to four values in a dossier. Therefore the Panel recommends assessing in such a case the magnitude of the effects of conservative assumptions in the inverse modelling procedure; if this effect is so large that it may explain the difference with the laboratory *DegT50* values, then it is considered justifiable to discard the $DegT50_{matrix}$ value of this field study.

Spatial variation in daily rainfall may be considerable on a scale of 100 km^2. As 10 mm is not a huge amount of rainfall, the time needed for 10 mm rainfall since application may also show considerable spatial variation at such a scale. Therefore it is advisable to measure cumulative rainfall between soil sampling times at the experimental field or at a distance of less than 1 km. Rainfall may not have been measured in available field dissipation studies. In such a case, the Panel recommends using rainfall data from weather stations at no more than 20 km distance from the experimental field. The applicant should make clear that there is no climatological barrier (e.g. mountains) between the rainfall station

and the experimental field. So the Panel proposes to ignore the uncertainty resulting from this aspect in this phase of the exposure assessment methodology.

The proposed procedure (Figures 9 and 10) considers only the possibility of time-step normalisation. FOCUS (2006) describes also another normalisation, i.e. rate normalisation. This procedure is based on the principle that the simulated daily transformation rate is corrected for differences between the actual temperature and moisture content and the temperature and moisture content at reference conditions (i.e. 20°C and pF = 2). Therefore this rate-normalisation procedure can only be used in fitting procedures that are based on daily simulation of this rate (e.g. ModelMaker or inverse modelling procedures based on models such as PELMO and PEARL). This will lead to more complex procedures than those proposed here but the Panel considers that rate normalisation is also acceptable for the procedures described in Figures 9 and 10. Especially when estimating the fast phase of the hockey-stick kinetics, rate normalisation could be an option because standard soil moisture and temperature corrections used for the time-step normalisation may be not adequate for substance near the soil surface.

4. Proposed guidance for analysing results of soil accumulation studies

In the context of Tiers 1 to 4 (Figure 1), the possible endpoints from soil accumulations studies are a $DegT50_{matrix}$ (of topsoil at 20°C and pF = 2) plus the F_{field} parameter describing a fast initial decline at the soil surface..

Soil accumulation studies can broadly be divided into two categories:

A. studies with only two to three samplings per year: one just before the yearly application, one just after the yearly application and one mid-year

B. studies in which each year a number of samplings has taken place.

The remainder of this section applies to type-A soil accumulation studies. If type-B studies contain enough samplings and if crop interception of the plant protection product was insignificant, the guidance for the field dissipation studies might be applicable.

Based on the experimental design of soil accumulation studies (two-three samplings per year), the Panel expects that it is impossible to estimate the fraction that penetrates into the soil separately from the $DegT50_{matrix}$.

The Panel considered the option to obtain the $DegT50_{matrix}$ by inverse modelling using a fixed, prescribed fraction that penetrates into the soil. This fixed fraction could be based on the calculations for the exposure scenario (e.g. using the crop interception tables proposed by FOCUS, 2000). Thus at least consistency would be assured: the $DegT50_{matrix}$ would be estimated on the basis of inverse modelling using the same fraction that penetrates into the soil as would be used later in the scenario calculations for the exposure assessment.

However, the Panel rejected this option for two reasons:

- the soil accumulation study may have been carried out under conditions that differ significantly from the required exposure scenario and thus it may be inappropriate to use the same fraction for strongly different situations (e.g. in the soil accumulation study application to full grown wheat crop and in required exposure scenario application to bare soil);

- this procedure prescribes the fraction that penetrates into the soil to the inverse modelling procedure; the true fraction in the soil accumulation study will differ from this prescribed fraction; therefore the inverse modelling procedure will return a $DegT50_{matrix}$ value with an unknown systematic error; such a $DegT50_{matrix}$ value cannot be simply compared in statistical tests to $DegT50_{matrix}$ values obtained from other sources (laboratory studies or field dissipation studies); so this makes it impossible to give such a $DegT50_{matrix}$ value an appropriate place in the stepped approach of Figure 2.

As a next option the Panel considered the possibility of estimating conservative $DegT50_{matrix}$ values (of top soil at 20°C and pF = 2) from soil accumulation studies (i.e. upper limits). An upper limit of the $DegT50_{matrix}$ is obtained by assuming a lower limit of the fraction of the dose that penetrates into the soil. This can be illustrated with the following example:

- on 1 June 2008 a dose of 1 kg/ha was sprayed onto a winter wheat crop; one year later 0.25 kg/ha was recovered from the soil

- if it is assumed that the whole dosage penetrated into the soil, the half-life under these field conditions is 0.5 year

- if it is assumed that only half of the dosage penetrated into the soil, the half-life under these field conditions is 1.0 year.

A lower limit of the fraction of the dose that penetrates into the soil implies an upper limit of the crop interception (and ignoring wash-off). The Panel is currently setting up a database of all available crop interception measurements which will be followed by an analysis of these data. The Panel hopes to be able to estimate reliable upper limits of the fraction intercepted by the crop (lower than the trivial 1.0) from this analysis at a later stage. The procedure might work in exceptional cases where the true $DegT50_{matrix}$ in soil accumulation studies is much shorter than in field dissipation studies.

If soil accumulation studies are carried out with spray applications to bare soil, another complication occurs: it will usually be impossible to derive from the study which fraction of the dose dissipated while most of the areic mass of the plant protection product was still in the top millimetres. If loss processes other than degradation in the soil in this top layer are ignored in the analysis, the $DegT50_{matrix}$ is overestimated which is not defensible.

The consequence from the above reasoning is that processes above and at the soil surface may have a large effect on the build-up of soil residues in soil accumulation studies, which makes it difficult to extrapolate results of soil accumulation studies to a range of conditions within the EU.

In view of the above complications, the Panel recommends not using type-A soil accumulation studies for deriving $DegT50_{matrix}$ values.

5. Proposed guidance for estimating model input parameters for the required exposure scenarios

5.1. Introduction

The guidance in Chapter 3 implies that each laboratory degradation rate study and each field dissipation study will lead to an estimated *DegT50*[8] at 20°C and pF = 2 for the topsoil layer. This guidance further implies that each field dissipation study will lead to an estimate of F_{field}.

So the next step is to provide guidance on how these data should be used to generate model input data for the required exposure scenario.

The guidance for estimation of model input parameters for the required exposure scenario will not include guidance for parameters derived from soil accumulation studies in view of the complications described in Chapter 4. This guidance will also not include estimation of model input parameters for Tiers 3 and 4 if these tiers are based on a relationship between the *DegT50* and soil properties such as the pH or clay content. So the guidance below is restricted to substances whose *DegT50* (at 20°C and pF = 2) is not a function of such soil properties.

5.2. Estimation of the geomean *DegT50* for the required exposure scenario from laboratory and field studies

Once *DegT50* values (top soils at 20°C and pF = 2) from laboratory and field studies are available, the estimation of the *DegT50* to be used as input for the required exposure scenario consists of two more steps (see Section 1.1):

(i) developing procedures for assessing the relevant population of *DegT50* values for the required exposure scenario

(ii) developing procedures for estimating reliably the geomean of the relevant population of *DegT50* values for the required exposure scenario.

So the first problem is to find the relevant population of *DegT50* values for the required exposure scenario. This problem has been addressed in the current EU leaching assessment. FOCUS (2000) developed nine EU groundwater scenarios. The *DegT50* is a very important input parameter for the scenario calculations. The current procedure is to calculate a geomean *DegT50* from either laboratory or field studies excluding only measurements with volcanic soils because their chemical and physical properties differ substantially from those of temperate mineral soils (e.g. their colloids are variably charged, having a positive charge at low pH and a negative charge at high pH and they have a lower bulk density and a higher hydraulic conductivity than most mineral soils). Soils from temperate regions outside the EU are considered also acceptable provided their pH, organic matter and clay contents are within the range of values to be expected for top soils in the EU. For field dissipation studies, it is additionally checked whether temperature and precipitation for the trial site are comparable to those in the EU where the assessed crop is grown. The geomean thus obtained is used for all nine groundwater scenarios. So it is implicitly assumed that a *DegT50* measured for any non-volcanic agricultural soil from temperate regions can be used to predict the *DegT50* for any non-volcanic agricultural soil within the EU. This assumption may be questioned of course: e.g. for a given substance it cannot be excluded that there are systematic differences in *DegT50* values of top soils (at 20°C and pF = 2) between the EU regulatory zones north and south or between the US and the EU

[8] This chapter deals with *DegT50* values obtained both in field and laboratory experiments. These will both be represented in this chapter by the acronym *DegT50* so without the 'matrix' suffix because it is not meaningful to use this suffix for laboratory studies and because it is assumed in this chapter that the values derived from the field studies are appropriate.

resulting from such factors as systematic differences in agricultural practices. The current Annex II data requirements for laboratory measurements of the *DegT50* state that studies with one soil are needed for the degradation route plus three for the degradation rate which sums up to four. With respect to the properties of the soils to be used, the current Annex II refers to SETAC (1995). This guideline specifies ranges of 2-5% organic matter, pH 5.5-7.5 and clay 10-25% for the degradation route. However, for the degradation rate studies, SETAC (1995) only states 'The additional soils … should cover a range of pH, organic matter and clay content typical of the regions where the pesticide will be used'. The draft version of the revised Annex II refers to OECD (2002a). This guideline prescribes only that 'the types of soils tested should be representative of the environmental conditions where use or release will occur'. So the geographical origin of the soil is not considered at all.

The Panel doubts whether such a crude approach for defining the relevant population of *DegT50* values for the required exposure scenario is defensible (e.g. NAFTA, 2006 prescribes a more subtle approach: i.e. to base the soil-selection procedure for field dissipation studies on GIS-based decision support models or on other GIS-based vulnerability assessment tools that account for the critical factors affecting pesticide dissipation). To underpin this crude approach, statistical analyses of existing *DegT50* data of a number of representative plant protection products are needed. On the other hand, the Panel is not aware of information that indicates that this crude approach is not defensible. Therefore the Panel proposes to accept this approach as a working hypothesis and to initiate in parallel activities to test this working hypothesis by careful analysis of relevant literature and other validated data.

Let us now assume that a relevant population of *DegT50* values (all at 20°C and pF = 2) is available and that it contains values from both laboratory studies and field dissipation studies. The problem is how to get to a geomean *DegT50*. The Panel recommends to calculate all geomeans using the bias-corrected geomean estimator described as D_4 in Appendix A.

Let us look back at the aim of the estimation of the *DegT50*: use of field dissipation studies (Step 2 in Figure 2) is only needed if Step 1 (i.e. using only laboratory *DegT50* values) does not result in acceptable risk to soil organisms. So within this Step 2 the notifier has to demonstrate that a possible risk does not exist. In the context of a tiered approach as in Figure 2, the information from higher steps should indicate a clear need to change the *DegT50* from Step 1. It means also that rejecting laboratory data from Step 1 in favour of field data from Step 2 is only defensible if there are convincing arguments to do so.

Beulke et al. (2000) reviewed 178 studies comparing breakdown in the field with that simulated by persistence models based on concepts used in models such as PELMO, PRZM and PEARL. The simulated percentage of initial concentration at the time of 50% measured loss was taken as the common criterion of model performance. The studies considered 27 plant protection products of which 26 were herbicides including simazine (25% of the 178 studies), atrazine (16%), propyzamide (10%), linuron (7%) and chlorotoluron (6%). The same soils were used in the laboratory test as in the field studies, this being an important aspect in making such comparisons. Simulated soil residues were overestimated in 72% of the 178 cases and underestimated in the other 28%. No measures were taken to exclude surface loss processes from the tests, and in a number of studies a rapid decline was observed early after application; examples were given of 36 such studies (20% thereof) with linuron, metolachlor, simazine, chlorotoluron and atrazine. Taking this into consideration, this would give about 60% overestimation versus 40% underestimation which is quite close to that expected on the hypothesis that degradation rates in the field and in the laboratory are equal at the same temperature and moisture.

For the regulatory exposure assessment, it is very important whether systematic differences between *DegT50* values from laboratory and field are mainly a property of the substance or not; Beulke et al. (2000) did not test this. If these differences are substance specific, they can be handled e.g. by using only the field geomean for substances where the field breakdown is faster and by using the geomean

of combinations of laboratory and field for substances where the two rates are similar. If these differences are not be substance specific, then they would have to be handled differently.

The Panel bases its guidance on the hypothesis of a substance-specific difference between *DegT50* values from the laboratory and the field, there being two arguments for this hypothesis: (i) different substances have different combinations of mechanisms of degradation in soil (e.g. chemical versus microbial) and (ii) laboratory studies are less suitable for measuring degradation of persistent substances because because their duration is restricted to 120 d (OECD, 2002b). Also regulatory practice is based on this hypothesis: for every new substance, field dissipation studies are carried out and default factors for differences between laboratory and field *DegT50* values are not considered acceptable.

The Panel proposes the flow chart shown in Figure 11. Box A tests whether the geomean laboratory *DegT50* is longer than 240 d. If so, there will be on average only 29% decline during the 120 d incubation of the OECD study, making it difficult to measure such low degradation rates. For such persistent substances, the Panel proposes not to perform a difference test between laboratory and field but to continue with the field values (box D). If the geomean laboratory *DegT50* is shorter than 240 d, box B tests the null hypothesis that the geomean *DegT50* values from laboratory and field are equal against the alternative hypothesis that the geomean DegT50 from the field is shorter (using the parametric multiplicative shift model described in Appendix A). As described before, the Panel considers the option of a geomean field *DegT50* that is longer than the geomean laboratory *DegT50* not to be meaningful, and so this is not considered (including this option would imply loss of statistical power for a given significance level).

The significance level will limit the probability of a false positive error (α). This is the error of accepting that *DegT50*'s from field studies are shorter than from laboratory studies when they are equal in reality; this has the consequence that concentrations of parent substances will be underestimated in soil exposure and leaching assessments. See appendix A for further explanation.

The normal statistical procedure is to set the significance level to 5%. Because of the small sample size (typically four or a few more studies) and the high variation of the resulting *DegT50*, this significance level will lead to a very low power in typical situations (about 35% was found simulating one such typical case). A low power (i.e. 1-β) means a high probability of a false negative error (i.e. β). This is the error of accepting no difference between *DegT50* from field studies and laboratory studies when those of the field are shorter in reality; this has the consequence that concentrations of parent substances will be overestimated in soil exposure and leaching assessments. In typical situations 65% of real differences will not be recognised by the test. This shows the limitations of the experimental design (small number of observations in combination with a high variation of the observations) for testing this hypothesis.

A simulation study of a typical case (see Appendix A) showed that a significance level of 25% will lead to equal probabilities of the false positive and false negative errors (so increase from 5 to 25% leads to decrease of 65% to 25% in the example discussed above). However, the regulatory consequences of false positive and false negative errors are quite different. A false positive error has the consequence that a plant protection product may be registered that does not fulfil the desired environmental criteria whereas a false negative error has the consequence that the notifier has to perform additional field studies to demonstrate that the *DegT50* in the field is indeed lower.

The choice of a significance level between 5 and 25% (e.g. 15%) is a risk management decision. Risk managers could consider accepting a higher significance level than 5% in the evaluation of existing dossiers. However, for future dossiers they could consider to use a significance level of 5% requiring a better experimental design (e.g. higher sample size or paired design) that will increase the power of the test.

If this null hypothesis is not rejected (box C), the Panel recommends pooling all the laboratory and field *DegT50* values and calculating the geomean (box F). If the null hypothesis is rejected, then we discard the laboratory studies and move to box D. In this box it is tested whether at least four field *DegT50* values are available. The four values are based on the data requirement for laboratory *DegT50* values in Annex II to Council Directive 91/414/EC. If this is indeed the case then the geomean field *DegT50* is calculated as the endpoint of this flow chart (box E). If less than four values are available, the uncertainty of the estimated geomean of the field *DegT50* values is considered too high and the Panel proposes to pool all the laboratory and field *DegT50* values (so back to box F).

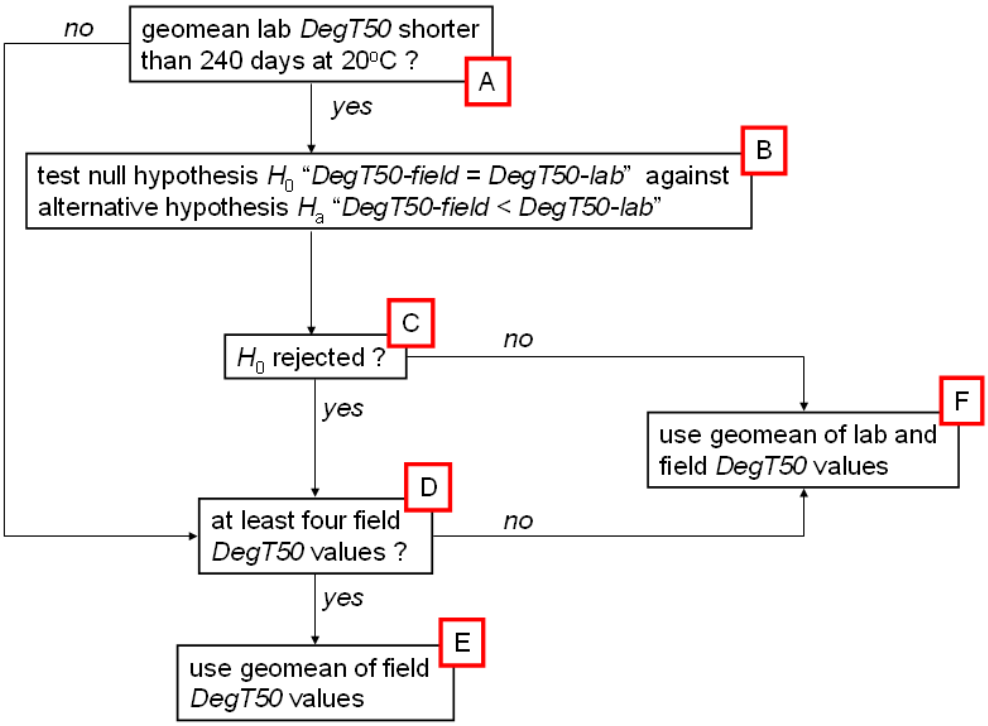

Figure 11: Flow chart for assessment of DegT50 values from laboratory and field dissipation studies. The letters A to E act as references to the corresponding boxes in the main text.

The calculation procedure for the geomean to be used in the exposure assessment is not straightforward because the geomean of the statistical population is needed and this may differ from the geomean of the sample population. In general, the uncertainty of the estimated geomean decreases with increasing sample size. To assess the magnitude of this uncertainty, we need an estimate of the standard deviation of the lognormal distribution of the *DegT50*. A first indication of the magnitude of this standard deviation can be obtained (Table 2). these values showing a range from 0.18 to 0.58 with a median of about 0.4. Most data sets are from one country. The median of the three data sets with soils from more than one country is 0.48. For the purpose of the EU risk assessment, the variability within the whole EU or within one of the three regulatory zones is relevant. Therefore a standard deviation of 0.5 is used to assess the uncertainty of the geomean of the statistical population.

Table 2: The dimensionless standard deviation of the natural logarithm of the *DegT50* as derived from literature data. The *DegT50* values in the laboratory studies are measurements and those from the field studies were obtained after normalisation.

Reference	*No. of soils*	*Substance*	*Origin of soils*	*Type of studies*	*Temperature + moisture content (FC = field capacity)*	*Standard deviation (-) of ln(DegT50) with CV between brackets*
Barrere et al. (1988)	29	propyzamide	France	lab	28°C at 0.25 kg/kg	0.41 (0.43)
Walker & Thompson (1977)	18	propyzamide	UK	lab	25°C at FC	0.34 (0.35)
Walker & Thompson (1977)	18	linuron	UK	lab	25°C at FC	0.45 (0.47)
Walker & Thompson (1977)	18	simazine	UK	lab	25°C at FC	0.18 (0.18)
Walker et al. (1983)	15	simazine	world	lab	20°C at 90% FC	0.48 (0.51)
Allen & Walker (1987)	18	metamitron	UK	lab	20°C at 330 hPa	0.40 (0.42)
Allen & Walker (1987)	18	metazachlor	UK	lab	20°C at 330 hPa	0.45 (0.47)
Hardy et al. (2003)	10	DKN	EU + US	field		0.38 (0.39)
Erzgräber et al. (2009)	12	unknown	EU	field		0.58 (0.63)

The confidence interval of the geomean of the statistical population was assessed by Monte Carlo simulations assuming a CV of the *DegT50* of 0.50 (corresponding with a standard deviation of the natural logarithm of 0.47). Each confidence interval was based on 50,000 draws. For four samples, the interval ranges from 66 to 143% (Figure 12), so the true value may be about 40% higher than the estimate. This uncertainty (which implicitly assumes a random set of experimental fields) must be taken into consideration in the further exposure assessments.

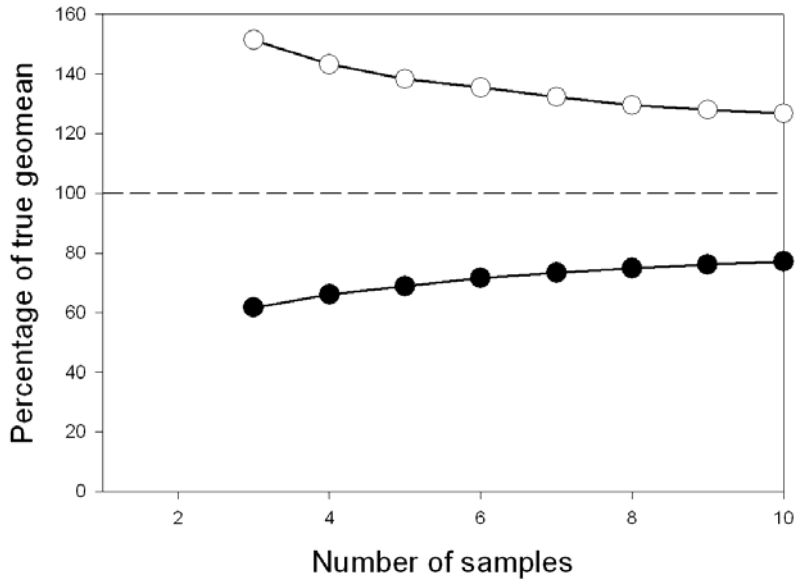

Figure 12: Confidence interval as percentage of the true value of the estimated geomean as a function of the sample size assuming a log-normal distribution with a CV of 0.5. The solid points are the 5th percentile and the open symbols are the 95th percentile. The geomean was estimated with estimator D_4 described in Appendix A.

5.3. Estimation of model input parameters describing the decline at the soil surface for the required exposure scenarios

As described above, the dissipation at the soil surface can be described with the parameter F_{field}. The estimation of this input parameter for the required scenario can be subdivided into:

A) does the observed fast decline also occur in the required exposure scenario?

B) which value of the input parameter is to be used?

For Step A, the Panel proposes that the fast surface decline is switched off (F_{field} = 0) unless the notifier provides plausible arguments to support the position that a fast initial decline is expected to occur in the required exposure scenario. Let us consider two examples: a case YES where this is indeed expected and a case NO where this is not expected. In case YES, the field dissipation study was in Germany and it showed a fast initial decline of 70% of the dose as a result of photodegradation. The required exposure scenario for this case was spraying onto bare soil in southern Europe in spring. In case NO, we have the same field study but now the required exposure scenario is spraying onto a crop with 80% deposition on the crop and 20% on the soil with most of the soil usually in the shadow of the plants.

For Step B, the Panel proposes to use the worst-case value of four accepted values. For example, four field dissipation studies show F_{field} values of 30, 40, 60 and 80% for studies in France, UK, Germany and Spain under normal agricultural use conditions. If less or more than four such values are available, the Panel proposes to use an estimate of the 12.5th percentile. This is approximately the same as the worst case of four values (ignoring the difference between a quantile of a sample population and the true population). It should be noted that processes responsible for the fast decline should be switched off in additional modelling studies.

Unlike the *DegT50*, for which the uncertainty was accounted for by selecting a scenario that represents a higher spatial percentile than the 80th (EFSA, 2010b), the uncertainty and spatial and temporal variability of the surface loss processes (F_{field}) were not considered in the scenario selection. The basis for the worst case of four is that, in EU regulatory practice, field dissipation studies with four soils are usually required.

5.4. Proposal for using the revised *DegT50* and F_{field} in the exposure assessments in the different tiers

Based on the previous sections, final values of *DegT50* and F_{field} are assumed to be available. The next step is to use these values in the exposure assessment for spray applications to annual crops under conventional and reduced tillage proposed by EFSA (2010a).

These values are relevant for Tiers 1 to 4 of Figure 1. The Panel proposes that a revised *DegT50* can be used for all these tiers. The Panel proposes to include the fast surface decline only in Tiers 2 or 4. Tiers 1 and 3 are based on simple analytical models (Figure 1) with no crop interception in Tier 1 and probably also no interception in Tier 3. It seems not in balance for Tiers 1 and 3 to exclude crop interception while including a fast surface decline (in contrast to Tiers 2 and 4).

The procedure for the parameterisation of the fast surface decline is given by the following four steps.

Step-1-F_{field} : run the model for the required simulation period (26 years for annual applications, 46 years for application every two years or 66 years for application every three years; see Section 3.3 of EFSA, 2010a) using a corrected dosage A_{cor} (kg/ha) given by

$$A_{cor} = A\ (1 - F_{field}) \qquad (12)$$

where A is the recommended dosage.

Step-2-F_{field} : calculate from this run (excluding the six 'warming-up' years; Section 3.3 of EFSA, 2010a) the average fraction of the dosage lost due to simulated volatilisation (F_{vola}) and runoff (F_{runoff}).

Step-3-F_{field} : extract from this run the application at which the all-time high concentration occurs.

Step-4-F_{field} : run the model a second time but now with a dosage given by

$$A_{cor} = A\ (1 - F_{field} + F_{vola} + F_{runoff}) \qquad (13)$$

for all applications except the application in the year where the all-time high concentration occurs; for this application use A as the dose.

The background to this procedure is as follows. Firstly there is the problem of 'double counting' of loss processes: the measured F_{field} may include runoff and volatilisation and so using F_{field} in combination with a model that already simulates volatilisation and runoff will lead to systematic underestimation of exposure concentrations. This is prevented by Eqn 13. Secondly there is the problem that the all-time high concentration would be systematically underestimated if Eqn 13 were always to be used because in reality the full dosage is sprayed.

If the application is onto a crop, part of the plant protection product will be intercepted by the crop and part will be deposited onto the soil. The areic mass intercepted by the crop will partly be washed off to the soil in the simulations (Section 3.6 of EFSA, 2010a). So also if there is crop interception, the Panel recommends using Eqn 13 (F_{field}) with A_{cor} being the sum of the areic masses sprayed onto crop and soil.

6. Usefulness of the proposed guidance for assessment of leaching to groundwater and surface water

The Panel considers the guidance proposals for estimating the $DegT50_{matrix}$ as described in Chapter 3 and Sections 5.2 also useful for assessment of leaching to groundwater (FOCUS, 2000) and surface water FOCUS (2001) because these proposals are not specific for the soil exposure assessment. Also the guidance for the estimation of the model input parameters describing the decline at the soil surface in Section 5.3 is not specific for soil exposure and can therefore be used for the leaching assessments.

However, the guidance for the initial-decline parameters to be used in the soil exposure scenario calculations in Section 5.4 contains elements that are specific to the soil exposure assessment and needs therefore to be modified as follows for leaching assessments:

1. if the leaching calculations are based on the convection-dispersion equation, then the proposed procedure of Step-1-F_{field} to Step-4-F_{field} should be followed with the modification that Eqn 13 can be used for all application years (so it is not necessary to make calculations with a full dose in one of the years); this is justifiable because leaching in such model calculations is a multi-year process;

2. if the leaching calculations include preferential flow, then the calculations have to be carried out assuming $F_{field} = 0$ because preferential flow events may take place shortly after application when almost the full dosage is still present.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The half-life for degradation in the top 30 cm of soil at 20°C and pF = 2 is an important input parameter for numerical models that simulate exposure of organisms in soil. For soil under conventional or reduced tillage, the main use of this half-life is to simulate the degradation rate in the topsoil (depths between ~1 and 30 cm). When deriving such a half-life from field dissipation and soil accumulation studies, appropriate measures have to be taken to ensure that the value obtained is not strongly influenced by processes in the top millimetres of soil (such as volatilisation and photodegradation).

2. Based on current knowledge and data commonly available in dossiers on plant protection products, it is impossible to estimate with enough certainty indirect photolysis rates of plant protection products in the top millimetres of soil under field conditions. Studies with sieved soils in the laboratory demonstrate that photodegradation in the field may occur but would be limited to the top 2 mm of soil. Furthermore there are uncertainties about assessing volatilisation for surface-applied compounds.

3. Current numerical models used for simulating behaviour of plant protection products in soil in the context of the EU regulatory exposure assessment are unable to describe satisfactorily the daily fluctuations of the soil temperature and of the volume fraction of water in the top millimetres of soil.

4. The parameters describing the relationship between the degradation rate coefficient in soil and the soil temperature (i.e. the Arrhenius activation energy) or the volume fraction of water in soil (i.e. the exponent *B*) show considerable variation between soils and plant protection products. This uncertainty results in a considerable uncertainty in $DegT50_{matrix}$ values obtained from field studies by inverse modelling assuming default values of the Arrhenius activation energy and the exponent *B*.

5. Assessment of $DegT50_{matrix}$ values based on field dissipation studies can be based on inverse modelling using the approach of normalised decline curves proposed by FOCUS (2006) following the flow charts (Figures 8 and 9). The normalised decline curves can be either described with the DFOP (double first-order kinetics) or Hockey-Stick models.

6. The Panel considers soil accumulation studies with only two to three soil samplings per year not suitable for estimating the $DegT50_{matrix}$ because the fraction of the dosage that penetrates to soil depths deeper than a few millimetres cannot be estimated with sufficient accuracy from the results of such studies.

7. Once appropriate *DegT50* values from laboratory and field studies are available, the estimation of the *DegT50* to be used as input for the required exposure scenario consists of two more steps: (i) assess the relevant population of *DegT50* values for the required exposure scenario, and (ii) estimate reliably the required statistical attribute (certain percentile or some mean value) based on this population. The Panel proposes basing the relevant population of *DegT50* values on the assumption that a *DegT50* measured for any non-volcanic agricultural soil from temperate regions can be used to predict the *DegT50* for any such soil within the EU. This assumption is a working hypothesis that has to be underpinned further. The type of attribute has to be consistent with the scenario-selection procedure which was based on taking the geomean *DegT50* value assuming a log-normal distribution. So the Panel recommends taking the geomean *DegT50* value. The estimation of the geomean *DegT50* of the population has to consider the uncertainty resulting from the limited number of samples in the sample population.

8. If the relevant population of *DegT50* values for a certain exposure scenario consist of a mixture of values obtained in the laboratory and in the field, the Panel recommends excluding the laboratory values only if the null hypothesis that laboratory and field values are equal is rejected. If the relevant

population of *DegT50* values for a certain exposure scenario consist of less than four values based on field studies, the Panel recommends using both laboratory and field values for estimating the geomean (also if this null hypothesis is rejected).

9. The Panel considers the guidance proposals for estimating *DegT50* values also useful for the assessment of leaching to groundwater and surface water because the main use of the *DegT50* values in these groundwater and surface water scenarios is the same as for the soil exposure assessment considered in this opinion (i.e. simulate the degradation rate for soil depths between 1 and 30 cm).

10. The *DegT50* in the soil has often a large effect on the exposure assessments for groundwater, aquatic organisms and soil organisms. Estimation of the *DegT50* is affected by many uncertainties, as discussed in the opinion. However, the Panel is of the opinion that the provision it has made for these uncertainties within the proposed procedures, together with the improved handling of processes in the top millimetres of soil, will mean that the *DegT50* of parent substances will be underestimated only for a small proportion of the substances. The Panel is also of the opinion that following this guidance document will improve the quality of these exposure assessments considerably and thus will help to protect the environment.

RECOMMENDATIONS

1. The Panel recommends the compilation of a database for all substances listed in Annex I which should contain information on all relevant and reliable *DegT50* values of agricultural top soils within the temperate regions at 20°C and pF = 2 to test the assumption that this *DegT50* does not vary systematically between geographical zones in the temperate regions for non-volcanic soils.

2. Should the notifier want to use results of field dissipation studies for estimating the $DegT50_{matrix}$ as an input parameter for exposure models, the Panel recommends incorporating the plant protection product to a depth of about 10 cm into the soil immediately after application.

3. Depending on substance properties and the application pattern, alternative options such as irrigation after spraying could also be appropriate when estimating the $DegT50_{matrix}$ if it is guaranteed that the compound was transported into the soil matrix.

4. The Panel recommends research be conducted to further improve the reliability of mechanistic models for simulating loss processes at the soil surface especially for photodegradation and volatilisation.

5. Some uncertainty has been addressed (Table 1 and Figure 12), but the Panel recognizes that further uncertainties exist and recommends that further work be done to evaluate their combined impact on the reliability of the exposure assessment.

6. In future exposure assessment methodologies, the Panel recommends including the uncertainty resulting from the use of the sample geomean to estimate the geomean of the statistical population, and intends to develop approaches for this in a forthcoming guidance.

REFERENCES

Allen R and Walker A,1987. The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. Pesticide Science, 18, 95-111.

Anderson JPE 1987. Handling and storage of soils for pesticide experiments. In: Pesticide effects on soil microflora. Somerville L, Greaves MP (Eds). Taylor and Francis, London, 45-60.

Barrere C, Bastide J and Coste CM 1988. Relations entre la vitesse de dégradation du propyzamide et les propriétés physicochimiques des sols. Weed Research, 28, 93-99.

Beulke S, Dubus IG, Brown CD, Gottesbüren B, 2000. Simulation of pesticide persistence in the field on the basis of laboratory data – a review. Journal of Environmental Quality, 29, 1371-1379.

Braud I, Noilhan J, Bessemoulin P and Mascart P, 1993. Bare-ground surface heat and water exchanges under dry conditions: observations and parameterization. Boundary-Layer Meteorology, 66, 173-200.

Bromilow RH, Evans AA and Nicholls PH, 1999. Factors affecting degradation rates of five triazole fungicides in two soil types, 2. Field studies. Pesticide Science 55, 1135-1142,

Ciani A, Goss K-U and Schwarzenbach RP, 2005. Light penetration in soil and particulate minerals.- European Journal of Soil Science, October 2005, 56, 561–574, doi: 10.1111/j.1365-2389.2005.00688.x

EFSA (European Food Safety Authority), 2007a. Opinion of the Scientific Panel on Plant protection products and their Residues on a request from the Commission related to the revision of Annexes II and III to Council Directive 91/414/EEC concerning the placing of plant protection products on the market - Fate and Behaviour in the Environment. The EFSA Journal, 448, 1-17.

EFSA (European Food Safety Authority), 2007b. Opinion on a request from EFSA related to the default *Q*10 value used to describe the temperature effect on transformation rates of pesticides in soil. The EFSA Journal, 622, 1-32.

EFSA (European Food Safety Authority), 2010a. Scientific opinion on outline proposals for assessment of exposure of organisms to substances in soil. EFSA Journal, 8(1):1442, 38 pp.

EFSA (European Food Safety Authority), 2010b. Selection of scenarios for exposure of soil organisms to plant protection products. EFSA Journal, 8(6): 1642, 82 pp.

EC (European Commission), 2000. Guidance Document on persistence in soil (SANCO/9188VI/1997 of 12 July 2000), 17 pp.

Erzgräber B, Gottesbüren B and Spickerma G, 2009. Identification and normalisation of pesticide degradation in field studies with strong bi-phasic decline pattern. Proceedings Conference 'Pesticide behaviour in soils, water & air , York, UK, 14-16.

Ferrari F, Trevisan M, and Capri E, 2003. Predicting and measuring environmental concentration of pesticides in air after soil application. Journal of Environmental Quality, 32, 1623–1633.

FOCUS, 1997. Soil Persistence Models and EU Registration, European Commission Document No. 7617/VI/96. URL: http://europa.eu.int/comm/food/plant/protection/evaluation/focus_en.htm.

FOCUS, 2000 "FOCUS groundwater scenarios in the EU review of active substances" - The report of the work of the Groundwater Scenarios Workgroup of FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe), Version 1 of November 2000. EC Document Reference Sanco/321/2000 rev.2, 202pp

FOCUS, 2001. FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2, 245 pp.

FOCUS, 2006. Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.

FOCUS, 2008. Pesticides in air: considerations for exposure assessment". Report of the FOCUS Working Group on Pesticides in Air, EC Document Reference SANCO/01572/2008 version 2.0, 327 pp.

Frank MP, Graebing P and Chib JS, 2002. Effect of soil moisture and sample depth on pesticide photolysis. Journal of Agricultural Food Chemistry, 50, 2607-2614.

Gottesbüren B, 1991. Konzeption, entwicklung, validierung des wissensbasierten herbizid-beratungssystems HERBASYS. Ph.D. Thesis University of Hannover, 212 pp.

Hardy IAJ, Jones RL, Allen R and Gatzweiler EW, 2003. Normalisation of field degradation data for soil temperature and moisture content for use in environmental risk assessment. Proceedings XII Symposium Pesticide Chemistry, Piacenza, Italy, 51-61.

Hebert VR and Miller GC, 1990. Depth Dependence of Direct and Indirect Photolysis on Soil Surfaces. Journal of Agricultural Food Chemistry, 38, 913-918.

Jackson RD, 1973. Diurnal changes in soil water content during drying. In: Field soil water regime Eds Bruce RR et al. SSSA Spec.Publ. no. 5. Soil Science Society of America, Madison, Wisconsin, 37-55.

Katagi T, 2004. Photodegradation of pesticides on plant and soil surfaces. Reviews of Environmental Contamination and Toxicology, 182,1-189.

Koorevaar P, Menelik G and Dirksen C, 1983. Developments in Soil Science 13: Elements of Soil Physics. Elsevier, Amsterdam, The Netherlands.

Miller PL and Chin YP, 2002. Photoinduced degradation of carbaryl in a wetland surface water. Journal of Agricultural Food Chemistry, 50, 6758-6785

NAFTA (North American Free Trade Agreement), 2006. NAFTA guidance document for conducting terrestrial field dissipation studies. Regulatory directive DIR2006-01, Pest Management Regulatory Agency, Ottawa, Ontario, 56 pp.

Nicholls PH, Briggs GG and Evans AA, 1984. The influence of water solubility on the movement and degradation of simazine in a fallow soil. Weed Research, 24, 37-49.

OECD (Organisation for Economic Co-operation and Development), 2002a. OECD guideline for the testing of chemicals. Phototransformation of chemicals on soil surfaces. Proposal for a new guideline. OECD, Paris, 16 pp.

OECD (Organisation for Economic Co-operation and Development), 2002b. OECD guideline for the testing of chemicals. Aerobic and anaerobic transformation in soil. Guideline nr 307, OECD, Paris, 17 pp.

Oliver R, 2010. Photodegradation in surface waters and soil: mechanisms and significance. Documentation map of 12th International Fresenius AGRO Conference 'Behaviour of pesticides in air, soil and water', Mainz, 10 pp.

Parkin TB and Kaspar TC, 2004. Temporal variability of soil carbon dioxide flux: effect of sampling frequency on cumulative carbon loss estimation. Soil Science Society of America Journal, 68, 1234–1241.

Rigg JC, Visser BF and Lehman HP, 1985. Nomenclature of derived quantities. Chemistry International, 7, 29-33.

Scorza Junior RP and Boesten JJTI, 2005. Simulation of pesticide leaching in a cracking clay soil with the PEARL model. Pest Management Science, 61, 432-448.

SETAC, (Society of Environmental Toxicology and Chemistry), 1995. Procedures for assessing the environmental fate and ecotoxicity of pesticides. Ed. Lynch MR. SETAC, Brussels, 54 pp.

Smelt JH, Dekker A and Leistra M, 1979. Effect of soil moisture condition on the conversion rate of oxamyl. Netherlands Journal of Agricultural Science, 27, 191-198.

Smit AAMFR, Van den Berg F and Leistra M, 1997. Estimation method for the volatilisation of pesticides from fallow soils. Environmental Planning Bureau series 2, DLO Winand Staring Centre, Wageningen, The Netherlands.

Steenpass C, Vanderborght J, Herbst M, Šimůnek J and Vereecken H, 2010. Estimating soil hydraulic properties from infra-red measurements of soil surface temperatures and TDR data (in press).

Tester M and Morris C, 1987. The penetration of light through soil. Plant, Cell and Environment, 10, 281-286.

Trapp S and McFarlane JC, 1995. Plant Contamination: Modelling and Simulation of Organic Chemical Processes, Lewis Publishers, Boca Raton.

Walker A, 1974. A simulation model for prediction of herbicide persistence. Journal of Environmental Quality,3, 396-401.

Walker A and Thompson JA, 1977. The degradation of simazine, linuron and propyzamide in different soils. Weed Research, 17, 399-405.

Walker A, Hance RJ, Allen JG, Briggs GG, Chen Y-L, Gaynor JD, Hogue EJ, Malquori A, Moody K, Moyer JR, W Pestemer W, Rahman A, Smith AE, Streibig JC, Torstensson NTL, Widyanto LS and Zandvoort R, 1983. EWRS herbicide-soil working group: collaborative experiment on simazine persistence in soil. Weed Research, 23, 373-383.

Zhixiong L, Nan C, Perdok UD and Hoogmoed WB, 2005. Characterisation of soil profile roughness. Biosystems Engineering, 91, 369-377.

Zobeck TM and Onstad CA,1987. Tillage and rainfall effects on random roughness: a review. Soil Tillage Research, 9, 1-20.

ABBREVIATIONS

DegT50	Half-life resulting from transformation of substance in the soil matrix
FOCUS	Forum for Co-ordination of pesticide fate models and their USe
PBT	Persistence Bioaccumulation Toxicity
PEC	Predicted Environmental Concentration
PEC_{SOIL}	Predicted Environmental Concentration in soil
PPP	Plant Protection Product; in the context of this opinion, the term 'plant protection products' is used for both the applied formulation and the active substances.
PPR Panel	Scientific Panel on Plant Protection Products and their Residues
TWA	Time-Weighted Average
F_{field}	rapidly dissipating fraction that is not related to degradation in the soil matrix

APPENDIX A

ESTIMATION OF THE MEDIAN FROM A LIMITED NUMBER OF DEGT50 STUDIES

TERMS OF REFERENCE AS PROVIDED BY EFSA-PPR WG "FATE / PERSISTENCE IN SOIL"

How to handle small data sets for degradation studies in soil, when using field or laboratory studies? Especially:

1. How to estimate the geomean (median) of log-normally distributed observations?
2. How to test the hypothesis that the geomean of the field studies is less than the geomean of the laboratory studies against the contrary?
3. How to test the hypothesis that the DegT50 value of a single field study is larger than expected by the distribution of results of all laboratory studies?

ASSESSMENT

To determine degradation rates in soil often only a few number of laboratory and/or field studies, e.g. 3 to 8, are performed. The obtained information allows only a restricted precision in the estimation of parameters used in the regulatory procedure for authorization.

The following report will evaluate different methods to estimate the median (50^{th} percentile) of the results of degradation half-life (*DegT50*) from typical laboratory and/or field studies and explores the resulting precision. A second aspect handles the assumption that laboratory studies are in general more conservative than field studies (and produce longer degradation times). The report also evaluates methods to confirm this hypothesis. A single field study might obtain a *DegT50* value which is larger than expected, when obtained by laboratory studies. A third aspect will test this situation to confirm or reject the unexpected high value.

7. Methods to estimate DegT50

7.1. General methods

Considering the results of N (laboratory) studies on *DegT50*, here "observations":

$$X_1, \ldots, X_N.$$

The following section will describe the general methods to estimate the median of such a sample. The methods are ordered by the different assumptions on the stochastic process, which generates the observations. For most methods their characteristics (bias, variance, mean square error) with small samples are not explicitly known or theoretically complicated to calculate. Therefore the next chapter will compare the different methods by a simulation study in a typical situation.

7.1.1. Direct estimation from the sample

Non-parametric methods will estimate the median from the ordered sample:

$$X_{(1)} \le X_{(2)} \le X_{(3)} \le \ldots \le X_{(n)} \le \ldots \le X_{(N-1)} \le X_{(N)}$$

by choosing the middle observation as estimator. This defines the

$$D_1 = \begin{cases} X_{\left(\frac{N+1}{2}\right)} & \text{when} \quad N \text{ is odd} \\ \frac{1}{2}\left(X_{\left(\frac{N}{2}\right)} + X_{\left(\frac{N}{2}+1\right)}\right) & \text{when} \quad N \text{ is even} \end{cases}$$ "classic Median estimator". (CM)

When the number of observations N is even, each value between $X_{\left(\frac{N}{2}\right)}$ and $X_{\left(\frac{N}{2}+1\right)}$ is allowed.

Most positive observations, like the *DegT50*s, follow a multiplicative model[9]. This means that the

$$D_2 = \begin{cases} X_{\left(\frac{N+1}{2}\right)} & \text{when} \quad N \text{ is odd} \\ \sqrt{X_{\left(\frac{N}{2}\right)} \cdot X_{\left(\frac{N}{2}+1\right)}} & \text{when} \quad N \text{ is even} \end{cases}$$ "multiplicative Median estimator" (MM)

is a more appropriate estimator. Both approaches give the same result for an odd number of observations. The multiplicative estimator yields a classic median estimator on logarithmic transformed observations after the transformation backwards.

The median estimator is robust against outliers, but shows in general greater variation than parametric approaches.

7.1.2. Estimation for log-normal distributed observations

Parametric approaches use the knowledge on the distribution of the observations to define more efficient estimators. In this section we assume that the observations follow a log-normal distribution, which is a reasonable and common used assumption for quantities that cannot become negative (e.g. half-lives and concentrations).

The log-normal distribution is applicable, when the log-transformed observations are symmetric and approximately normal distributed. The logarithmic transformation as well as the normal distribution can be seen as basic models for observations on a multiplicative scale. They are used when no further information contradicts them. A reference for the log-normal distribution is Aitchison and Brown (1957), Johnsen, Kotz and Balakrishnan (1994).

The Maximum-Likelihood (ML) estimator uses the log-transformed observations to estimate the parameters, i.e. the mean and variance, of the underlying normal distribution.

$$\hat{\mu} = \frac{1}{N}\sum_{n=1}^{N} \ln\left(X_n\right)$$

$$\hat{\sigma}^2 = \frac{1}{N-1}\sum_{n=1}^{N} \left(\ln\left(X_n\right) - \hat{\mu}\right)^2$$

Here the usual bias corrected estimator for the variance is used.

The relationship between these parameters and the median of the log-normal distribution

$$\text{Med}(X) = \exp(\mu)$$

can be used to define a further estimator. The

[9] This means that changes in the experimental conditions are more likely to cause relative (multiplicative) than absolute (additive) changes in the result.

$$D_3 = \exp(\hat{\mu}) = \exp\left(\frac{1}{N}\sum_{n=1}^{N}\ln(X_n)\right) = \sqrt[N]{\prod_{n=1}^{N} X_n} \qquad \text{“Geomean estimator” (GM)}$$

Unfortunately this estimator is biased due to the non-linear back transformation.

$$E(\exp(\hat{\mu})) = \exp\left(\mu + \frac{\sigma^2}{2N}\right) = \text{Med}(X)\cdot\exp\left(\frac{\sigma^2}{2N}\right)$$

The bias correction yields in the

$$D_4 = \exp\left(\hat{\mu} - \frac{\hat{\sigma}^2}{2N}\right) \qquad \text{“corrected Geomean estimator” (CG)}$$

(Johnsen, Kotz and Balakrishnan, 1994).

The following table shows all computation steps to estimate the median of *DegT50* values from laboratory studies using the bias Corrected Geomean estimator:

Calculations	**Laboratory studies**				
	Cont. No. i	***DegT50* values** A x_i	**logarithmic *DegT50* values** D $l_i = \ln(x_i)$=	**deviation from mean μ** G $d_i=(l_i-\mu_{lab})$=	**squared deviation from mean μ** H d_i^2=
	1	x_1= 30	l_1= 3.401	d_1= -0.309	d_1^2= 0.0954
	2	x_2= 51	l_2= 3.932	d_2= 0.222	d_2^2= 0.0492
	3	x_3= 49	l_3= 3.892	d_3= 0.182	d_3^2= 0.0331
	4	x_4= 46	l_4= 3.829	d_4= 0.119	d_4^2= 0.0141
	5	x_5= 68	l_5= 4.220	d_5= 0.510	d_5^2= 0.2596
	6	x_6= 54	l_6= 3.989	d_6= 0.279	d_6^2= 0.0778
	7	x_7= 15	l_7= 2.708	d_7= -1.002	d_7^2= 1.0039
Number of studies	B **N**= 7				
Degrees of freedom	C $df_{lab} = N-1$= 6				
Sum over all studies	E $L = \Sigma_i l_i$ = 25.970			I $D^2 = \Sigma_i d_i^2$ = 1.5330	
Mean of logarithmic values	F $\mu_{lab} = L/N$ = 3.710				
Variance of logarithmic values				J $\sigma_{lab}^2 = D^2/df_{lab}$ = 0.2555	
Standard deviation of logarithmic values				$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$ = 0.5055	
Correction				K $S = \sigma_{lab}^2/(2 \cdot N)$ = 0.0183	
Corrected μ			L $U = \mu_{lab} - S$ = 3.692		
Corrected Geomean Estimator for the Median			M **Median** = exp(U) = 40.1		

Computations steps:

A List all **values x_i** (indexed by i) of *DegT50* for the existing **laboratory studies**

B Identify the **number N** of existing laboratory studies

C Determine the number of **degrees of freedom df_{lab}**, this is the number of studies N reduced by 1: **$df_{lab} = N-1$**

D Compute the **natural logarithm l_i** of each *DegT50*-value: **$l_i = \ln(x_i)$**

E Calculate the **sum L of all logarithmic values**: **$L = \Sigma_i l_i$**

F Calculate the **mean μ_{lab}** of the logarithmic values of DegT50 of laboratory studies: **$\mu_{lab} = L/N$**

G Calculate the **deviation d_i** between each logarithmic value from the mean: **$d_i = (l_i - \mu_{lab})$**

H Compute the **square d_i^2** of each deviation.

I Calculate the **sum D^2 of all squared deviations: $D^2 = \Sigma_i d_i^2$**

J Calculate the **variance σ_{lab}^2** of the logarithmic values of *DegT50* of laboratory studies by dividing the sum of squared deviances by the degrees of freedom: **$\sigma_{lab}^2 = D^2/df_{lab}$**. The square root gives the standard deviation: **$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$**

K Calculate the **correction S** by dividing the variance by two times the number of studies: **$S = \sigma_{lab}^2/(2 \cdot N)$**

L **Correct** the mean by the correction value: **$U = \mu_{lab} - S$**

M **Transform** the corrected mean back to the original scale by applying the exponential function: **Median** = exp(U). This gives the bias-corrected Geomean as estimator of the Median.

8. Methods to compare two experimental results

The following section will consider two groups of studies on *DegT50* with N respectively M observations

Laboratory studies: $X_1, \ldots, X_N$.

Field studies: $Z_1, \ldots, Z_M$.

To compare these experiments it is not necessary to estimate the medians beforehand.

We use statistical tests to confirm the general hypothesis that

H: "*DegT50* in field studies" ("fld", Z)
is lower than "DegT50 from laboratory studies" ("lab", X)

with the null hypothesis that

H_0: "*DegT50* in field studies" ("fld", Z)
is equal to "*DegT50* from laboratory studies" ("lab", X)

Table 3: Interpretation of the test results

Reality	***Result of the statistical test***		***Remarks:***
	(T=1) Test confirms H: "fld" < "lab"	(T=0) Test holds H_0: "fld" = "lab"	
"fld" < "lab"	**Correct positive:** P = 1-ß, Power (Sensitivity)	False negative: P = ß	← Typical example: $DegT50_{fld}$=100d $DegT50_{lab}$=150d
"fld" = "lab"	False positive: P < α (=10%)	**Correct negative** P=1-α (Specificity)	← Esp. no difference

The false-positive error is controlled by the significance level α (=10%) of the test. This means that the probability "That the test will confirm that $DegT50_{fld}$ in field studies is lower than in lab studies, when the $DegT50_{lab}$ in lab studies is equal" is smaller than α (=10%), while the power is the probability of a correct positive result. In the simulation study the power is calculated for a real difference of a typical situation: $DegT50_{fld}$=100 d in field studies against $DegT50_{lab}$=150 d in laboratory studies. The false positive error may result in the assumption of a too short DegT50 in the regulatory process and in consequence an underestimation of exposure concentrations.

100%-power is the probability of the false-negative error that is to state "that the $DegT50_{fld}$ of field studies is equal, when in reality the $DegT50_{lab}$ of laboratory studies is larger". This error is normally not controlled by a statistical test. The false negative error may result in the assumption of a too long DegT50 in the regulatory process and overestimation of exposure concentrations. Industry might be forced in this situation to provide more field studies to demonstrate that the DegT50 in the field is indeed lower.

8.1. Student's t-test to compare the locations of two distributions

For log-normal distributed observations it is obvious to assume that the difference between the two distributions is described by a factor

$$\mathcal{Q}(X) = c \cdot \mathcal{Q}(Z)$$

This implies that the median value DegT50 values of laboratory experiments Median(X) is c-times the median of the results of field experiments Median(Z), while the coefficient of variation (CV) is equal for both. To test, if c < 1, we can use Student's t-test for the means of the log-transformed observations.

$$H : E(\ln(Z)) < E(\ln(X)) \quad \text{against} \quad H_0 : E(\ln(Z)) = E(\ln(X))$$

A significant exceedance of the arithmetic mean of ln(X) compared to the arithmetic mean of ln(Z) will contradict our null hypothesis

$$t = \frac{\mu_{lab} - \mu_{fld}}{\sigma \cdot \sqrt{\frac{1}{N} + \frac{1}{M}}} \qquad \text{with} \qquad \sigma^2 = \frac{(N-1) \cdot \sigma_{lab}^2 + (M-1) \cdot \sigma_{fld}^2}{N + M - 2}$$

The t-test to the significance level α is defined as

$$\text{Reject } H_{0,} \text{ if:} \qquad t > t_{N+M-2,\,1-\alpha} \quad (T = 1)$$

For a correct assumption of log-normally distributed samples this test procedure is precise also for small sample sizes. Otherwise the test will not exactly meet the chosen significance level.

The following table shows all computations to perform the test to confirm that the *DegT50* values from field studies are shorter than from laboratory studies. **Example 1:**

Calculations	**Laboratory studies**				
	Cont. No. i	**DegT50 values** A x_i	**logarithmic DegT50 values** D $l_i = \ln(x_i)$=	**deviation from mean μ** G $d_i=(l_i-\mu_{lab})$=	**squared deviation from mean μ** H d_i^2=
	1	x_1= 30	l_1= 3.401	d_1= -0.309	d_1^2= 0.0954
	2	x_2= 51	l_2= 3.932	d_2= 0.222	d_2^2= 0.0492
	3	x_3= 49	l_3= 3.892	d_3= 0.182	d_3^2= 0.0331
	4	x_4= 46	l_4= 3.829	d_4= 0.119	d_4^2= 0.0141
	5	x_5= 68	l_5= 4.220	d_5= 0.510	d_5^2= 0.2596
	6	x_6= 54	l_6= 3.989	d_6= 0.279	d_6^2= 0.0778
	7	x_7= 15	l_7= 2.708	d_7= -1.002	d_7^2= 1.0039

Number of studies	B **N**= 7		
Degrees of freedom	C df_{lab} = N–1= 6		
Sum over all studies		E **L**= $\Sigma_i l_i$ = 25.970	I $D^2 = \Sigma_i d_i^2$ = 1.5330
Mean of logarithmic values		F μ_{lab}= L/N = 3.710	
Variance of logarithmic values			J σ_{lab}^2= D^2/df_{lab} = 0.2555
Standard deviation of logarithmic values			$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$ = 0.5055

Calculations	**Field studies**				
	Cont. No. j	**DegT50 values** K z_j	**logarithmic DegT50 values** N $k_j = \ln(x_j)$=	**deviation from mean μ** Q $c_j=(l_j-\mu_{fld})$=	**squared deviation from mean μ** R c_j^2=
	1	z_1= 31	k_1= 3.434	c_1= 0.214	c_1^2= 0.0459
	2	z_2= 23	k_2= 3.135	c_2= -0.084	c_2^2= 0.0071
	3	z_3= 25	k_3= 3.219	c_3= 0.001	c_3^2= 0.0000
	4	z_4= 22	k_4= 3.091	c_4= -0.129	c_4^2= 0.0166

Number of studies	L **M**= 4		
Degrees of freedom	M df_{fld} = M–1= 3		
Sum over all studies		O **K**= $\Sigma_j k_j$ = 12.879	S $C^2 = \Sigma_j c_j^2$ = 0.0696
Mean of logarithmic values		P μ_{fld}= K/M = 3.220	
Variance of logarithmic values			T σ_{fld}^2= C^2/df_{fld} = 0.0232
Standard deviation of logarithmic values			$\sigma_{fld} = \sqrt{\sigma_{fld}^2}$ = 0.1523

Comparison between laboratory and field studies				
Sum of degrees of freedom			U **df** = df_{lab}+ df_{fld} =	9
Sum of reciprocal sample sizes	V **h** = (1/N)+(1/M) =	0.3929		
Difference between means	W **A** = $\mu_{lab} - \mu_{fld}$ =	0.490		
Sum of squared deviations			X **B** = $D^2 + C^2$=	1.6026
Combined variance of logarithmic values			Y σ^2 = B/df =	0.1781
Standard deviation of the difference between the means			Z **s** = $\sqrt{h \cdot \sigma^2}$ =	0.2645
Statistic of Student's t-test			AA **t** = A/s=	1.8532
Significance level of the test α (as given in the procedure)			AB **α** =	10%
Upper 1–α quantile of t-distribution with df degrees of freedom			(see table 2:) AC $t_{df,1-\alpha}$ =	1.3830

AD Is Student's t-statistic **t** larger than the t-quantile $t_{df,1-\alpha}$ **?**

☒ **YES**: $t > t_{df,1-\alpha}$	→ Test confirms that field studies show shorter DegT50 than laboratory studies	☐ **NO**: $t \leq t_{df,1-\alpha}$	→ Observations do not contradict the hypothesis that field studies show equal DegT50 as laboratory studies

The following table shows all computations to perform the test to confirm that the *DegT50* values from field studies are shorter than from laboratory studies. **Example 2:**

Calculations	**Laboratory studies**									
	Cont. No. i	**DegT50 values** A x_i		**logarithmic DegT50 values** D $l_i = \ln(x_i)$=		**deviation from mean μ** G $d_i=(l_i-\mu_{lab})$=		**squared deviation from mean μ** H d_i^2=	
	1	x_1=	30	l_1=	3.401	d_1=	-0.309	d_1^2=	0.0954
	2	x_2=	51	l_2=	3.932	d_2=	0.222	d_2^2=	0.0492
	3	x_3=	49	l_3=	3.892	d_3=	0.182	d_3^2=	0.0331
	4	x_4=	46	l_4=	3.829	d_4=	0.119	d_4^2=	0.0141
	5	x_5=	68	l_5=	4.220	d_5=	0.510	d_5^2=	0.2596
	6	x_6=	54	l_6=	3.989	d_6=	0.279	d_6^2=	0.0778
	7	x_7=	15	l_7=	2.708	d_7=	-1.002	d_7^2=	1.0039
Number of studies		B **N**=	7						
Degrees of freedom		C $df_{lab} = N-1$=	6						
Sum over all studies				E $L = \Sigma_i l_i$ =	25.970			I $D^2 = \Sigma_i d_i^2$ =	1.5330
Mean of logarithmic values				F $\mu_{lab} = L/N$ =	3.710				
Variance of logarithmic values								J $\sigma_{lab}^2 = D^2/df_{lab}$ =	0.2555
Standard deviation of logarithmic values								$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$ =	0.5055

Calculations	**Field studies**									
	Cont. No. j	**DegT50 values** K z_j		**logarithmic DegT50 values** N $k_j = \ln(x_j)$=		**deviation from mean μ** Q $c_j=(l_j-\mu_{fld})$=		**squared deviation from mean μ** R c_j^2=	
	1	z_1=	41	k_1=	3.714	c_1=	0.122	c_1^2=	0.0148
	2	z_2=	49	k_2=	3.892	c_2=	0.300	c_2^2=	0.0900
	3	z_3=	32	k_3=	3.466	c_3=	-0.126	c_3^2=	0.0159
	4	z_4=	27	k_4=	3.296	c_4=	-0.296	c_4^2=	0.0876
Number of studies		L **M**=	4						
Degrees of freedom		M $df_{fld} = M-1$=	3						
Sum over all studies				O $K = \Sigma_j k_j$ =	14.367			S $C^2 = \Sigma_j c_j^2$ =	0.2083
Mean of logarithmic values				P $\mu_{fld} = K/M$ =	3.592				
Variance of logarithmic values								T $\sigma_{fld}^2 = C^2/df_{fld}$ =	0.0694
Standard deviation of logarithmic values								$\sigma_{fld} = \sqrt{\sigma_{fld}^2}$ =	0.2635

Comparison between laboratory and field studies				
Sum of degrees of freedom			U **df** = $df_{lab} + df_{fld}$ =	9
Sum of reciprocal sample sizes	V **h** = (1/N)+(1/M) =	0.3929		
Difference between means	W **A** = $\mu_{lab} - \mu_{fld}$ =	0.118		
Sum of squared deviations			X **B** = $D^2 + C^2$=	1.7414
Combined variance of logarithmic values			Y σ^2 = B/df =	0.1935
Standard deviation of the difference between the means			Z $s = \sqrt{h \cdot \sigma^2}$ =	0.2757
Statistic of Student's t-test			AA **t** = A/s=	0.4290
Significance level of the test α (as given in the procedure)			AB α =	10%
Upper 1–α quantile of t-distribution with df degrees of freedom			(see table 2:) AC $t_{df,1-\alpha}$ =	1.3830

AD Is Student's t-statistic **t** larger than the t-quantile $t_{df,1-\alpha}$?

☐ **YES**: $t > t_{df,1-\alpha}$	→ Test confirms that field studies show shorter DegT50 than laboratory studies	☒ **NO**: $t \leq t_{df,1-\alpha}$	→ Observations do not contradict the hypothesis that field studies show equal DegT50 as laboratory studies

Computations steps:

A List all **values x_i** (indexed by i) of DegT50 for the existing **laboratory studies**

B Identify the **number N** of existing laboratory studies

C Determine the number of **degrees of freedom df_{lab}**,
this is the number of studies N reduced by 1: **$df_{lab} = N-1$**

D Compute the **natural logarithm l_i** of each DegT50-value: **$l_i = \ln(x_i)$**

E Calculate the **sum L of all logarithmic values**: **$L = \Sigma_i\, l_i$**

F Calculate the **mean μ_{lab}** of the logarithmic values of DegT50 of laboratory studies: **$\mu_{lab} = L/N$**

G Calculate the **deviation d_i** between each logarithmic value from the mean: **$d_i = (l_i - \mu_{lab})$**

H Compute the **square d_i^2** of each deviation.

I Calculate the **sum D^2 of all squared deviations: $D^2 = \Sigma_i\, d_i^2$**

J Calculate the **variance σ_{lab}^2** of the logarithmic values of DegT50 of laboratory studies by dividing the sum of squared deviances by the degrees of freedom: **$\sigma_{lab}^2 = D^2/df_{lab}$.** The square root gives the standard deviation: **$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$**

K List all **values z_j** (indexed by j) of DegT50 for the existing **field studies**

L Identify the **number M** of existing field studies

M Determine the number of **degrees of freedom df_{fld}**,
this is the number of studies M reduced by 1: **$df_{fld} = M-1$**

N Compute the **natural logarithm k_j** of each DegT50-value: **$k_j = \ln(z_j)$**

O Calculate the **sum K of all logarithmic** values: $K = \Sigma_j\, k_j$

P Calculate the **mean μ_{fld}** of the logarithmic values of DegT50 of field studies**: $\mu_{fld} = K/M$**

Q Calculate the **deviation c_j** between each logarithmic value from the mean: **$c_j = (k_j - \mu_{fld})$**

R Compute the **square c_j^2** of each deviation.

S Calculate the **sum C^2 of all squared deviations: $C^2 = \Sigma_j\, c_j^2$**

T Calculate the **variance σ_{fld}^2** of the logarithmic values of DegT50 of laboratory studies by dividing the sum of squared deviances by the degrees of freedom: **$\sigma_{fld}^2 = C^2/df_{fld}$.** The square root gives the standard deviation: **$\sigma_{fld} = \sqrt{\sigma_{fld}^2}$**

U Calculate the **sum df of the degrees of freedom**
of laboratory and field studies: **df** = $df_{lab} + df_{fld}$

V Calculate the **sum h of the reciprocal sample sizes**
of laboratory and field studies: **h** = (1/N)+(1/M)

W Calculate the **difference A of means of logarithmic DegT50 values**
from laboratory and field studies: **A** = $\mu_{lab} - \mu_{fld}$

X Calculate the **sum B of the squared deviances** of laboratory and field studies: **B** = $D^2 + C^2$

Y Calculate the **combined variance σ^2** of logarithmic DegT50 values
of laboratory and field studies: **σ^2** = B/df

Z Calculate the **standard deviation s of the difference of means**: **s** = $\sqrt{h \cdot \sigma^2}$ =

AA Calculate **Student's t-statistic** by dividing the difference of means by their standard deviation: **t** = A/s

AB Confirm the given **significance level α** of the test procedure: **α**

AC Determine the corresponding **$1-\alpha$ quantile $t_{df,1-\alpha}$ of Student's t-distribution**
with df degrees of freedom from the table: **$t_{df,1-\alpha}$**

AD **Compare the t-statistic t with the $1-\alpha$ quantile $t_{df,1-\alpha}$** to decide if**: $t > t_{df,1-\alpha}$ or: $t \le t_{df,1-\alpha}$**

Table 4: Quantiles of Student's t-distribution

Significance level	α =	5%	10%	15%	20%	25%
	$1-\alpha$ =	95%	90%	85%	80%	75%
Degrees of freedom		$t_{df,1-\alpha}$ =				
df=	2	2.9200	1.8856	1.3862	1.0607	0.8165
	3	2.3534	1.6377	1.2498	0.9785	0.7649
	4	2.1318	1.5332	1.1896	0.9410	0.7407
	5	2.0150	1.4759	1.1558	0.9195	0.7267
	6	1.9432	1.4398	1.1342	0.9057	0.7176
	7	1.8946	1.4149	1.1192	0.8960	0.7111
	8	1.8595	1.3968	1.1081	0.8889	0.7064
	9	1.8331	1.3830	1.0997	0.8834	0.7027
	10	1.8125	1.3722	1.0931	0.8791	0.6998
	11	1.7959	1.3634	1.0877	0.8755	0.6974
	12	1.7823	1.3562	1.0832	0.8726	0.6955
	13	1.7709	1.3502	1.0795	0.8702	0.6938
	14	1.7613	1.3450	1.0763	0.8681	0.6924
	15	1.7531	1.3406	1.0735	0.8662	0.6912
	16	1.7459	1.3368	1.0711	0.8647	0.6901
	17	1.7396	1.3334	1.0690	0.8633	0.6892
	18	1.7341	1.3304	1.0672	0.8620	0.6884
	19	1.7291	1.3277	1.0655	0.8610	0.6876
	20	1.7247	1.3253	1.0640	0.8600	0.6870

8.2. Student's t-test to confirm that a single observations is outside a given distribution

The test if a single observation corresponds to a given distribution can be handled in the same setting with:

Z_1 (M=1), additional single observation.

The test evaluates if a single observation Z_1 is larger than predicted by the distribution of the laboratory studies (X_n).

$$H: E(\ln(Z_1)) > E(\ln(X)) \quad \text{against} \quad H_0: E(\ln(Z_1)) = E(\ln(X))$$

Therefore we can use the same setting as in chapter 2.1.1 replacing the results of field studies by a single observation.

$$t = \frac{\ln(Z_1) - \mu_{lab}}{\sqrt{\sigma^2_{lab} \cdot \left(\frac{1}{N} + 1\right)}} > t_{N-1,\,95\%}$$

If the difference between the logarithm of the additional observation and the mean of the logarithmic values of the laboratory studies is larger than predicted, this will contradict the null hypothesis.

If more than one additional observation should be tested simultaneously a modified test has to be applied.

The following table shows all computations to perform the test to confirm that an additional *degT50* value obtained with either the DFOP or HS model is larger than expected from laboratory studies

Example 1:

Calculations	**Laboratory studies**				
	Cont. No. i	**DegT50 values** A x_i	**logarithmic DegT50 values** D $l_i = \ln(x_i)$=	**deviation from mean μ** G $d_i=(l_i-\mu_{lab})$=	**squared deviation from mean μ** H d_i^2=
	1	x_1= 30	l_1= 3.401	d_1= -0.309	d_1^2= 0.0954
	2	x_2= 51	l_2= 3.932	d_2= 0.222	d_2^2= 0.0492
	3	x_3= 49	l_3= 3.892	d_3= 0.182	d_3^2= 0.0331
	4	x_4= 46	l_4= 3.829	d_4= 0.119	d_4^2= 0.0141
	5	x_5= 68	l_5= 4.220	d_5= 0.510	d_5^2= 0.2596
	6	x_6= 54	l_6= 3.989	d_6= 0.279	d_6^2= 0.0778
	7	x_7= 15	l_7= 2.708	d_7= -1.002	d_7^2= 1.0039

Number of studies	B **N**= 7		
Degrees of freedom	C df_{lab} = N–1= 6		
Sum over all studies	E **L**= $\Sigma_i l_i$ = 25.970	I D^2= $\Sigma_i d_i^2$ =	1.5330
Mean of logarithmic values	F μ_{lab}= L/N = 3.710		
Variance of logarithmic values		J σ_{lab}^2= D^2/df_{lab} =	0.2555
Standard deviation of logarithmic values		$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$ =	0.5055

Calculations	**High value obtained from field experiment**		
	Cont. No.	**DegT50 value**	**logarithmic DegT50 value**
	j= 1	K z_1= 121	L k_1= $\ln(z_1)$= 4.796

Comparison between laboratory studies and single value				
Sum of reciprocal sample sizes	M **h** = (1/N)+ 1 =	1.1429		
Difference between means	N **A** = $k_1 - \mu_{lab}$ =	1.0858		
Standard deviation of the difference between the means			O **s** = $\sqrt{h \cdot \sigma_{lab}^2}$ =	0.5404
Statistic of Student's t-test			P **t** = A/s=	2.0093
Significance level of the test α (as given in the procedure)			Q **α** =	5%
Upper 1–α quantile of t-distribution with df degrees of freedom		(see table 2:)	R $t_{df\_lab,1-\alpha}$ =	1.9432

S Is Student's t-statistic **t** larger than the t-quantile $t_{df\_lab,1-\alpha}$ **?**

☒ **YES:** $t > t_{df\_lab,1-\alpha}$	→ Test confirms that single value shows longer DegT50 than expected from laboratory studies	☐ **NO:** $t \leq t_{df\_lab,1-\alpha}$	→ Single value does not contradict the hypothesis that it is resulting from the distribution of laboratory values

The following table shows all computations to perform the test to confirm that an additional *degT50* value obtained with either the DFOP or HS model is larger than expected from laboratory studies.

Example 2

Calculations	**Laboratory studies**									
	Cont. No. i	**DegT50 values** A x_i		**logarithmic DegT50 values** D $l_i = \ln(x_i)$=		**deviation from mean μ** G $d_i=(l_i-\mu_{lab})$=		**squared deviation from mean μ** H d_i^2=	
	1	x_1=	30	l_1=	3.401	d_1=	-0.309	d_1^2=	0.0954
	2	x_2=	51	l_2=	3.932	d_2=	0.222	d_2^2=	0.0492
	3	x_3=	49	l_3=	3.892	d_3=	0.182	d_3^2=	0.0331
	4	x_4=	46	l_4=	3.829	d_4=	0.119	d_4^2=	0.0141
	5	x_5=	68	l_5=	4.220	d_5=	0.510	d_5^2=	0.2596
	6	x_6=	54	l_6=	3.989	d_6=	0.279	d_6^2=	0.0778
	7	x_7=	15	l_7=	2.708	d_7=	-1.002	d_7^2=	1.0039

Number of studies	B **N**=	7			
Degrees of freedom	C df_{lab} = N–1=	6			
Sum over all studies		E **L**= $\Sigma_i l_i$ =	25.970	I $D^2 = \Sigma_i d_i^2$ =	1.5330
Mean of logarithmic values		F μ_{lab}= L/N =	3.710		
Variance of logarithmic values				J $\sigma_{lab}^2 = D^2/df_{lab}$ =	0.2555
Standard deviation of logarithmic values				$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$ =	0.5055

Calculations	**High value obtained from field experiment**				
	Cont. No.	**DegT50 value**		**logarithmic DegT50 value**	
	j= 1	K z_1=	73	L $k_1 = \ln(z_1)$=	4.290

Comparison between laboratory studies and single value				
Sum of reciprocal sample sizes	M **h** = (1/N)+ 1 =	1.1429		
Difference between means	N **A** = $k_1 - \mu_{lab}$ =	0.5805		
Standard deviation of the difference between the means			O **s** = $\sqrt{h \cdot \sigma_{lab}^2}$ =	0.5404
Statistic of Student's t-test			P **t** = A/s=	1.0742
Significance level of the test α (as given in the procedure)			Q **α** =	5%
Upper 1–α quantile of t-distribution with df degrees of freedom			(see table 2:) R $t_{df\_lab,1-\alpha}$ =	1.9432

S Is Student's t-statistic **t** larger than the t-quantile $t_{df\_lab,1-\alpha}$ **?**

☐ **YES:** $t > t_{df\_lab,1-\alpha}$	→ Test confirms that single value shows longer DegT50 than expected from laboratory studies	☒ **NO:** $t \leq t_{df\_lab,1-\alpha}$	→ Single values do not contradict the hypothesis that it is resulting from the distribution of laboratory values

Computation steps:

A List all **values x_i** (indexed by i) of DegT50 for the existing **laboratory studies**

B Identify the **number N** of existing laboratory studies

C Determine the number of **degrees of freedom df_{lab}**, this is the number of studies N reduced by 1: **$df_{lab} = N-1$**

D Compute the **natural logarithm l_i** of each DegT50-value: **$l_i = \ln(x_i)$**

E Calculate the **sum L of all logarithmic values**: **$L = \Sigma_i l_i$**

F Calculate the **mean μ_{lab}** of the logarithmic values of DegT50 of laboratory studies: **$\mu_{lab} = L/N$**

G Calculate the **deviation d_i** between each logarithmic value from the mean: **$d_i = (l_i - \mu_{lab})$**

H Compute the **square d_i^2** of each deviation.

I Calculate the **sum D^2 of all squared deviations: $D^2 = \Sigma_i d_i^2$**

J Calculate the **variance σ_{lab}^2** of the logarithmic values of DegT50 of laboratory studies by dividing the sum of squared deviances by the degrees of freedom: **$\sigma_{lab}^2 = D^2/df_{lab}$.** The square root gives the standard deviation: **$\sigma_{lab} = \sqrt{\sigma_{lab}^2}$**

K List the **additional DegT50-value z_1** obtained with either the DFOP or HS model

L Compute the **natural logarithm k_1** of the additional DegT50-value: **$k_1 = \ln(z_1)$**

M Calculate the **sum h of reciprocal sampling size and 1**: **$h = (1/N) + 1$**

N Calculate the **difference A between additional logarithmic value and mean** of laboratory studies: **$A = z_1 - \mu_{lab}$**

O Calculate the **standard deviation s of the difference** between additional logarithmic value and mean of laboratory studies: **$s = \sqrt{h \cdot \sigma_{lab}^2}$**

P Calculate **Student's t-statistic** by dividing the difference of means by their standard deviation: **$t = A/s$**

Q The significance level is set to: **$\alpha = 5\%$**

R Determine the corresponding **$1-\alpha$ quantile $t_{df\_lab,1-\alpha}$ of Student's t-distribution with df_{lab} degrees of freedom** from the table: **$t_{df\_lab,1-\alpha}$**

S **Compare the t-statistic t with the $1-\alpha$ quantile $t_{df\_lab,1-\alpha}$** to decide if**: $t > t_{df\_lab,1-\alpha}$ $t \leq t_{df\_lab,1-\alpha}$**

9. Simulation study on realistic examples (Beulke et al 2000)

Only a few theoretical results are known for the given estimators and test procedures. Most facts need strong assumptions on the underlying distributions and/or a larger sample size. To examine the characteristics in the situation of small sample sizes we apply the given estimators and test procedure to a reasonable typical case.

Beulke et al (2000) compared the degradation times of field experiments (observed) with laboratory experiments (simulated) from 178 published studies. They found the following distribution of ratios between pesticide concentrations in simulations and observation at DegT50 of field experiments (Beulke et al 2000, Fig.3). Table 5 converts these ratios into the ratio between DegT50 values of laboratory and field studies.

Table 5: Distribution of ratios between DegT50 from laboratory and field experiments based on data of Beulke et al (2000)

Ratio of concentrations c at $DegT50_{fld}$ (c_{fld} is 50% of the initial concentration)		***Ratio of DegT50[(1)] [%]***			***Frequency of studies***	***Cumulative frequency of studies***
c_{fld} / c_{lab}	$r = c_{lab} / c_{fld}$	$DegT50_{lab} / DegT50_{fld}$				
2.000 – ∞	0.000 – 0.500	0%	–	50%	4.5%	4.5%
1.750 – 2.000	0.500 – 0.571	50%	–	55%	1.7%	6.2%
1.500 – 1.750	0.571 – 0.667	55%	–	63%	3.4%	9.6%
1.250 – 1.500	0.667 – 0.800	63%	–	76%	7.3%	16.9%
1.000 – 1.250	0.800 – 1.000	76%	–	100%	11.2%	28.1%
0.800 – 1.000	1.000 – 1.250	100%	–	147%	28.1%	56.2%
0.667 – 0.800	1.250 – 1.500	147%	–	241%	25.3%	81.5%
0.571 – 0.667	1.500 – 1.750	241%	–	519%	13.5%	95.0%
0.500 – 0.571	1.750 – 2.000 (=max)	519%	–	∞	5.1%	100%

(1) = ln(0.5)/ln(r/2)

Roughly half of the substances showed a 50% exceeded degradation time in laboratory studies compared to field studies. As a typical situation we set the median degradation time of field studies to DegT50=100 d and for laboratory studies to DegT50=150 d, which is 50% exceeded.

The coefficient of variation of the distributions of DegT50 values from laboratory and field studies is set equal to 0.5. Because of the uncertainty of this parameter the value was varied from 0.25 to 0.75 (chapter 3.2). The number of studies was varied from 3 up to 10 to show the influence of the number of observations on the result. The typical number was set to N=M=5.

The characteristics of all estimators are described with

- Bias, average deviation of the estimator from the true value: $\mathrm{Bias}(D) = \mathrm{E}(D - \mathrm{Median})$
- Standard deviation of the estimator: $\mathrm{Std}(D)$
- Mean Squared Error (MSE): $\mathrm{MSE}(D) = \mathrm{E}(D - \mathrm{Median})^2 = \mathrm{Std}^2(D) + \mathrm{Bias}^2(D)$

The power of all tests is calculated for the given example: $\mathrm{Power}(T) = P(T = 1)$

In the example, the hypothesis that "DegT50 in field studies (100 d) is lower than in laboratory studies (150 d)" is valid and should be detected.

9.1. Typical log-normal experiments

In this section we assume a typical setting for DegT50 experiments of pesticides.

- **Laboratory studies:**
  Median = 150.1 [d], CV=0.499, log-normally distributed, N=5 observations

- **Field trials (failing the null hypothesis):**
  Median = 100.1 [d], CV=0.499, log-normally distributed, M=5 observations

We simulated 50000 replications and calculated, for all replications, all estimators D_1 to D_4 and the test T_1. The simulations were done with SAS-IML programming language.

Table 6: Simulation results for a typical set of laboratory studies on DegT50

	Average	*Bias*		*Std*		*MSE*	*5th percentile*		*95th percentile*		*Power*
		abs	*rel*	*abs*	*rel*		*abs*	*rel*	*abs*	*rel*	
Estimator (only lab studies)	***[d]***	***[d]***	***[%]***	***[d]***	***[%]***	***[d²]***	***[d]***	***[%]***	***[d]***	***[%]***	***[%]***
D1: classic Median (CM)	155	4.8	3.2%	39.8	26.5%	1603	99	66%	227	151%	
D2: multiplicative Median (MM)	155	4.8	3.2%	39.8	26.5%	1603	99	66%	227	151%	
D3: Geomean (GM)	153	3.2	2.1%	32.7	21.8%	1081	106	70%	212	141%	
D4: corrected Geomean (CG)	150	-0.2	-0.1%	32.1	21.4%	1030	103	69%	207	138%	
Tests (lab vs. fields)											
T2: Student's t											50%

Relative values are compared with true value = 150.01 d

In this regular situation the Maximum-Likelihood estimator of the parameters of the log-normal distribution with bias correction for the median gives, for theoretical reasons, optimal results: Lowest expected deviation of the estimator from the true value (Bias), lowest standard deviation of the estimator and lowest Mean Square Error (MSE), as a combination of bias and standard deviation. More remarkable is that the differences between all methods are minor. The bias varies between 0% and 3%, the standard deviation varies between 32 and 40d. The 5th percentile is about 2/3 of the true value and we need an uncertainty factor of about 1.5 to be 95% sure that the corrected estimator (1.5 ·CG) exceeds the true value. But in about 5% of the estimations the corrected value will be more than two times the true value.

For odd sample sizes there is no difference between the classic (CM) and multiplicative median (MM) estimator. But for all even samples sizes the multiplicative approach gives smaller bias values (Table 5).

The parametric t-test shows only a power of 50% to recognize the difference between experimental trials (median=150.1 d) and field studies (median=100.1 d), which is an indicator of an insufficient experimental setting, e.g. the number of studies is too small to detect the typical difference regarding the given variation between the studies.

Table 7: Simulation results to compare the Classic and Multiplicative Median estimator

Estimator (only lab studies)	*N*	*Average*	*Bias*		*Std*		*MSE*	*5th percentile*		*95th percentile*	
			abs	*rel*	*abs*	*rel*		*abs*	*rel*	*abs*	*rel*
		[d]	*[d]*	*[%]*	*[d]*	*[%]*	*[d²]*	*[d]*	*[%]*	*[d]*	*[%]*
D1: classic Median (CM)	4	158	7.6	5.1%	41.3	27.5%	1763	100	67%	233	155%
	6	155	5.0	3.4%	34.4	22.9%	1210	106	70%	217	144%
	8	154	3.5	2.4%	29.9	19.9%	907	110	73%	207	138%
	10	153	2.8	1.8%	27.0	18.0%	734	113	75%	200	134%
D2: multiplicative Median (MM)	4	155	5.0	3.3%	40.4	26.9%	1657	98	66%	229	152%
	6	154	3.8	2.5%	34.1	22.7%	1177	105	70%	215	143%
	8	153	2.8	1.9%	29.8	19.8%	893	109	73%	206	138%
	10	152	2.3	1.5%	26.9	17.9%	726	112	75%	200	133%

Relative values are compared with true value = 150.01 d

9.2. Influence of the coefficient of variation

In this section we assume again the typical log-normal setting for DegT50 observations, but varying the CV value.

- **Laboratory studies:**
  Median = 150.1 [d], CV variable, log-normally distributed, N=5 observations

- **Field trials (failing the null hypothesis):**
  Median = 100.1 [d], CV as in experimental trials, log-normally distributed, M=5 observations

We simulated 50000 replications and calculated ,for all replications, the estimators D_2, D_4 and the test T_1.

Table 8: Simulation results to compare the influence of varying CVs

Estimator (only lab studies)	*CV*	*Average*	*Bias*		*Std*		*MSE*	*5th percentile*		*95th percentile*		*Power*
			abs	*rel*	*abs*	*rel*		*abs*	*rel*	*abs*	*rel*	
	[%]	*[d]*	*[d]*	*[%]*	*[d]*	*[%]*	*[d²]*	*[d]*	*[%]*	*[d]*	*[%]*	*[%]*
D2: multiplicative Median (MM)	25%	151	1.3	0.8%	20.0	13.4%	403	121	81%	187	124%	
	50%	155	4.7	3.2%	39.7	26.5%	1599	99	66%	228	152%	
	75%	160	10.1	6.8%	59.0	39.4%	3588	84	56%	269	180%	
D4: corrected Geomean (CG)	25%	150	0.0	0.0%	16.5	11.0%	272	124	83%	179	119%	
	50%	150	0.1	0.0%	32.1	21.4%	1031	104	69%	208	138%	
	75%	150	0.1	0.1%	46.0	30.7%	2120	88	59%	235	156%	
Tests (lab vs. fields)												
T2: Student's t	25%											88%
	50%											51%
	75%											36%

Relative values are compared with true value = 150.01 d

All results in sections 3.1 to 3.2 depend on the distributional assumptions. But the most important parameter is the Coefficient of Variation (CV), which describes the ratio between the standard deviation and the mean of the observations.

For a fixed median an increasing CV value means increasing variation of the observations, which results in more variation in the process of estimation. Looking at the uncertainty factor,

$$UF = \frac{1}{5^{th}\ perc.}$$

a CV of 0.249 needs a correction of UF=1.2, CV=0.499 needs UF=1.5 and CV=0.749 needs UF=1.7 to ensure with 95% confidence that the increased, corrected Geomean estimator (CG) exceeds the true value.

Regarding the test of differences between the experiments and field observations an increased CV describes higher variation or a "relative" smaller difference between the two studies. The correct detection of the difference (power) is more difficult for a higher variation and decreases from 88% to only 29%.

9.3. Influence of the number of observations

In this section we assume again the typical log-normal setting for DegT50 observations, but vary the number of observations.

- **Laboratory studies:**
  Median = 150.1 [d], CV=0.499, log-normally distributed, N=varying

- **Field trials (failing the null hypothesis):**
  Median = 100.1 [d], CV=0.499, log-normally distributed, M=N

We simulated 50000 replications and calculated, for all replications, the estimators D_2, D_4 and the test T_1.

There is a clear positive effect on larger sample sizes. The differences between the methods become smaller, the necessary correction factor decreases from 1.7 (N=3) to 1.35 (N=10) for the corrected Geomean and the power of the test increases from about 37% to 72%.

Table 9: Simulation results for a regular log-normal experiment with varying sample sizes

Estimator (only lab studies)	*CV*	*Average*	*Bias*		*Std*		*MSE*	*5th percentile*		*95th percentile*		*Power*
			abs	*rel*	*abs*	*rel*		*abs*	*rel*	*abs*	*rel*	
	[%]	*[d]*	*[d]*	*[%]*	*[d]*	*[%]*	*[d²]*	*[d]*	*[%]*	*[d]*	*[%]*	*[%]*
D2: multiplicative Median (MM)	3	158	7.8	5.2%	51.1	34.1%	2674	89	60%	253	168%	
	4	155	5.0	3.3%	40.4	26.9%	1657	98	66%	229	152%	
	5	155	4.7	3.2%	39.8	26.5%	1604	99	66%	227	152%	
	6	154	3.8	2.5%	34.1	22.7%	1177	105	70%	215	143%	
	7	153	3.5	2.3%	33.6	22.4%	1140	105	70%	214	143%	
	8	153	2.8	1.9%	29.8	19.8%	893	109	73%	206	138%	
	9	153	2.8	1.9%	29.7	19.8%	890	109	73%	206	137%	
	10	152	2.3	1.5%	26.9	17.9%	726	112	75%	200	133%	
D4: corrected Geomean (CG)	3	150	0.2	0.2%	42.0	28.0%	1765	92	62%	228	152%	
	4	150	0.0	0.0%	35.9	24.0%	1291	99	66%	215	143%	
	5	150	-0.3	-0.2%	32.0	21.3%	1021	103	69%	207	138%	
	6	150	0.1	0.1%	29.2	19.5%	853	107	72%	203	135%	
	7	150	-0.1	-0.1%	26.9	17.9%	724	110	73%	198	132%	
	8	150	0.0	0.0%	25.1	16.8%	632	113	75%	194	130%	
	9	150	0.0	0.0%	23.8	15.8%	564	114	76%	192	128%	
	10	150	-0.1	-0.1%	22.5	15.0%	506	116	77%	190	126%	
Tests (lab vs. fields)												
T2: Student's t	3											37%
	4											44%
	5											50%
	6											56%
	7											61%
	8											65%
	9											69%
	10											72%

Relative values are compared with true value = 150.01 d

9.4. Influence of the significance level α on the power of Student's t-test

In this section we assume again the typical log-normal setting for DegT50 observations, but vary the significance level of the Student's t-test (T_2).

- **Laboratory studies:**
  Median = 150.1 [d], CV=0.499, log-normally distributed, N=5, α varying
- **Field trials (failing the null hypothesis):**
  Median = 100.1 [d], CV=0.499, log-normally distributed, M=N

We use the student's t-test to confirm the general assumption

H: "$DegT50_{fld}$ in field studies" **is lower than** "$DegT50_{lab}$ from laboratory studies"

against the null hypothesis that

H_0: "$DegT50_{fld}$ in field studies" is larger or equal than
"$DegT50_{lab}$ from laboratory studies"

We simulated 50000 replications and calculated, for all replications, the power of the Student's t-test (T_1). This is the probability of the test to confirm the (true) assumption.

In this simulation consisting of two alternatives: "$DegT50_{fld}$=100d / $DegT50_{lab}$=150d" vs. "$DegT50_{fld}$=$DegT50_{lab}$=150d", the power is equal to the sensitivity of the test to detect the difference, while 100%−α is the specificity of the test to detect the equality (Table 10).

Table 10: Sensitivity and specificity of the test procedure to confirm the difference between DegT50fld =100d and DegT50lab =150d

α [%]	***power*** *(=sensitivity)* [%]	***1-α*** *(=specificity)* [%]	***Youden index*** *(=sens.+spec.-100%)* [%]
0%	0%	100%	0%
5%	35%	95%	30%
10%	50%	90%	40%
15%	61%	85%	46%
20%	69%	80%	49%
25%	75%	75%	50%
30%	80%	70%	50%
35%	83%	65%	48%
40%	86%	60%	46%
45%	89%	55%	44%
50%	91%	50%	41%
55%	93%	45%	38%
60%	95%	40%	35%
65%	96%	35%	31%
70%	97%	30%	27%
75%	98%	25%	23%
80%	99%	20%	19%
85%	99%	15%	14%
90%	99%	10%	9%
95%	100%	5%	5%
100%	100%	0%	0%

Sensitivity and specificity (100%-α) are antagonists. To find an optimal balance between them we have to specify the possible consequences of false decisions.

The false-positive error is controlled by the significance level α of the test. This means that the probability "That the test will confirm that $DegT50_{fld}$ in field studies is lower than in laboratory studies, when the $DegT50_{lab}$ in laboratory studies is equal" is smaller than α. The false positive error may result in the assumption of a too short DegT50 in the regulatory process and, as a consequence, an underestimation of exposure concentrations.

100%-power is the probability of the false-negative error. That is to state "that the $DegT50_{fld}$ of field studies is equal, when in reality the $DegT50_{lab}$ of laboratory studies is larger". This error is normally not controlled by a statistical test. The false negative error may result in the assumption of a too long DegT50 in the regulatory process and overestimation of exposure concentrations. Industry might be forced in this situation to provide more field studies to demonstrate that the DegT50 in the field is indeed lower. A usual statistical test will focus on avoiding a false confirmation of the hypothesis and choose a low level of the false positive error (resp. a high specificity). Up to a significance level of α=25% the false positive error is smaller than the false negative error. Beyond that level the false positive error will be higher than the false negative, which is not wanted regarding the consequences of the decisions.

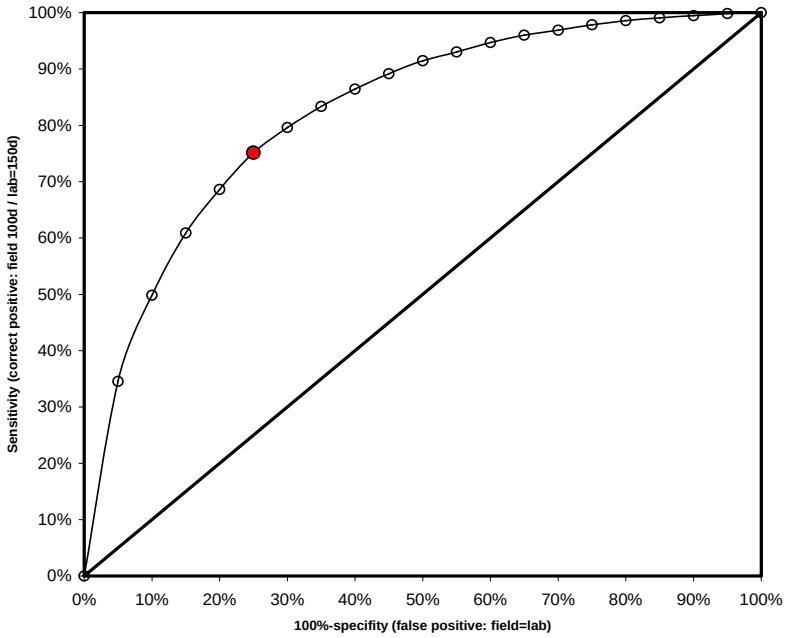

Figure 13: ROC to confirm the difference between $DegT50_{fld}$ =100d and $DegT50_{lab}$ =150d

REFERENCES

Aitchison J and Brown IAC, 1957. The lognormal distribution. Cambridge University Press, Cambridge.

Beulke S, Dubus IG, Brown CD and Gottesbüren B, 2000. Simulation of Pesticide Persistence in the Field on the Basis of Laboratory Data – A Review. Journal of Environmental Quality, 29, 1371-1379.

Johnson NL, Kotz S and Balakrishnan N, 1994. Continuous univariate distributions, volume 1, 2nd. Ed. Wiley, New York.